Wisconsin Mercury Deposition Network Summary Report

1995-1997

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Acknowledgments
We would like to thank Mike Halsted for help during the formatting of the document as well as the WDNR staff that made useful suggestions on the content and format of the paper.

Wisconsin Mercury Deposition Network Summary Report

Volume 2
Publication #: PUB-AM-302-99
Publication Date: November 1999
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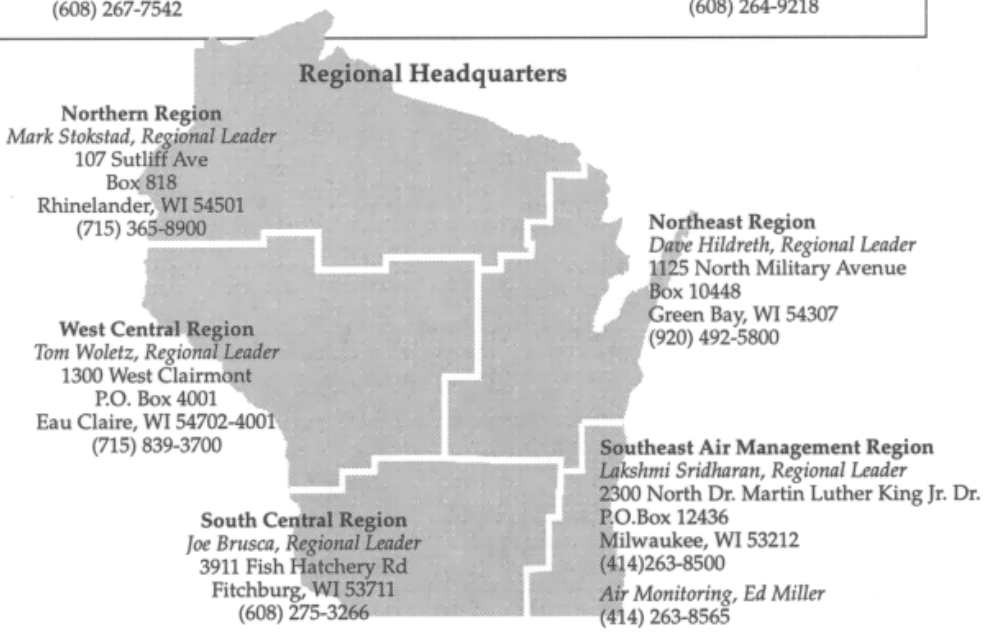

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EXECUTIVE SUMMARY

The State of Wisconsin is interested in assessing the amount of atmospheric mercury deposited to the environment on a statewide basis. From 1995-1997, a statewide network of seven passive IVL mercury monitors collected a weekly bulk sample that was analyzed for its mercury content. Sites with at least 75% data capture ($n \geq 39$) were included in the statistical analysis portion of the report.

Weekly, seasonal and annual deposition values were calculated for each site during the three years. Total annual deposition values were variable and ranged from 6 to 16 $\mu g/m^2$/yr, with the greatest total occurring in 1996. Mean weekly deposition during the three year period varied between 0.1 and 0.35 $\mu g/m^2$/week, and there were no statistically significant differences in mean weekly deposition within a given year. The annual statewide mean weekly deposition values during the three year period were also not significantly different (mean ± 95% confidence interval) (0.25 ± 0.04, 0.25 ± 0.06, and 0.2 ± 0.06 $\mu g/m^2$/year), respectively. Mean seasonal deposition varied greatly with maxima occurring either in the spring or summer.

Precipitation weighted concentrations (PWC) were calculated for each site during the 1995-1997 monitoring period as well. On a statewide basis, 70% of the PWC means ranged from 10 to 20 ng/L. These values are similar to those measured in other states in the northcentral United States. Annual precipitation weighted means for the entire state (mean ± 95% confidence interval) (15.8 ± 2.7, 13.7 ± 5.5, and 11.5 ± 2.7 ng/L), respectively, were not statistically different ($p \leq 0.22$).

Three sites (Trout Lake, Wildcat Mountain and Lake Geneva) were compared over the three year period. Seasonal and annual differences in deposition and concentration values were evident. Except for high spring concentration and deposition values in 1996 at Wildcat and Lake Geneva, the three sites had relatively similar results. A comparison of three consecutive years of weekly mercury deposition values showed that a majority of the deposition at these sites occurred in the late spring and early summer.

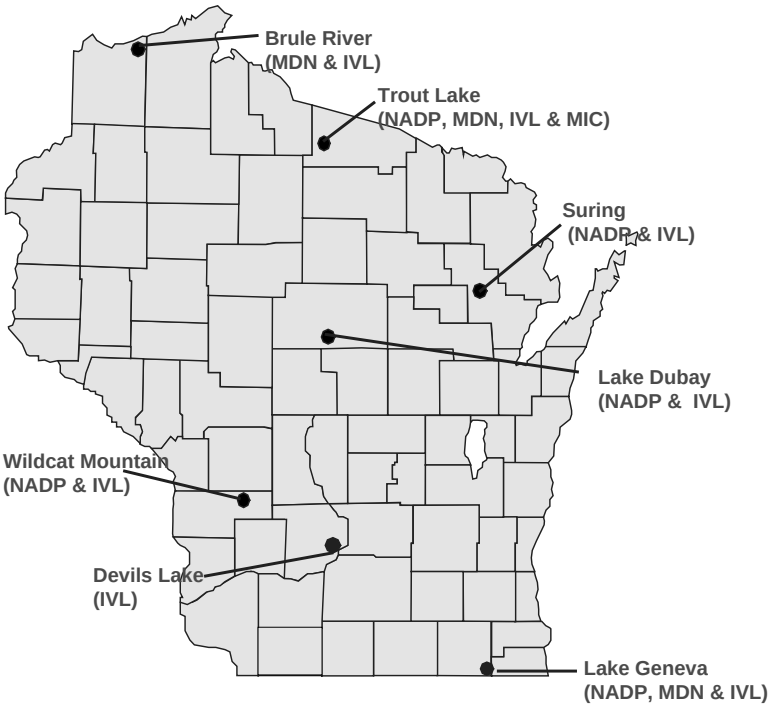
WIVL concentration and deposition results were compared to collocated national Mercury Deposition Network (MDN) (wet-only) monitor results. Results yielded by the two monitors were very similar at both Trout Lake and Lake Geneva.

INTRODUCTION

Atmospheric deposition is thought to be a major pathway for mercury to enter the Wisconsin environment. In the chain of events from the initial volatilization of mercury or suspension of mercury compounds into the atmosphere to its accumulation in fish-eating organisms, the washing of mercury from the atmosphere by various forms of precipitation constitutes a critical step in the availability of this toxin. This step provides a logical point at which to monitor mercury levels and determine loading rates to local environments due to wet deposition. A comprehensive program to quantify mercury concentration in rain and to develop deposition loading is critical to developing a better understanding of the atmospheric deposition pathway.

The Wisconsin Mercury Deposition Monitoring Network (WMDN) is a network of seven monitoring stations, operated by the Wisconsin Department of Natural Resources (WDNR), designed to collect information on the total (wet and dry) mercury deposition to the environment (Fig. 1a). The network makes use of a passive sampler based on a design used successfully in Sweden by the Swedish Environmental Research Institute (Institutet för Vatten- och Luftvårdsforskning (IVL)).

Figure 1a



Wisconsin Atmospheric Deposition Monitoring Sites

The monitoring objectives for the WMDN include developing trend information for the temporal and spatial distribution of mercury in Wisconsin; developing baseline data to evaluate effectiveness of the future mercury control strategies; and characterizing environmental exposures to mercury. Previous reports have discussed the initial development and testing of the passive sampler, as well as early data collected from the sampler (1). This report will detail three years of monitoring results from 1995 through 1997. It covers a transition period for the sampling network that includes modification to the sampler and the development of analysis capabilities within the Wisconsin State Laboratory of Hygiene (SLOH).

The WMDN is one of two routine monitoring programs in Wisconsin. A second program, the National Mercury Deposition Network (MDN), collects wet-only deposition as part of a national program. Data collected by the WMDN is intended to complement data gathered at four National (MDN) sites located in Wisconsin. A third monitoring program designed for collecting events sampling was started but never fully developed before funding limits forced the program's end.

MERCURY BACKGROUND

MERCURY THE ELEMENT

Mercury is a naturally occurring element with physical and chemical properties useful in a number of applications. It is unique among metals because it may re-volatize after deposition. Mercury is used for medicinal, electrical, agricultural, and scientific purposes as well as for other products. The heavy metal conducts electricity and finds application in electrical switches, batteries, and lighting elements. Physically, mercury has a melting point of -38°C, an atomic weight of 200.6 AMU, and valences of 1 and 2. It has a high specific gravity (13.5 g/cc) and is the only metal that is liquid at room temperature. These properties make it useful in measuring devices such as barometers and manometers.

Chemically mercury can act as a catalyst for reactions. The metal can also inhibit reaction of enzymes and poison biological systems. Ionic mercury (Hg^{2+}) has a strong affinity for sulfur and forms stable complexes with amino acids containing sulfur such as cysteine, cystine, and methionine. The poisonous properties of mercury make it useful as a biocide and as a preservative in paints.

Many of mercury's anthropogenic uses result in its emission to the atmosphere as a by-product in a number of processes. Some of the sources of man-made atmospheric mercury include:

(1) the heating and burning of fossil fuels and ores, coal and coke making processes and carbon black manufacturing.
(2) industrial emissions, cement production, lime manufacturing, and metal extraction processes
(3) paints
(4) agricultural uses (fungicides)
(5) solid waste incineration and the evasion of land fill gases
(6) dental amalgams
(7) sewage treatment plant effluents

Secondary anthropogenic emissions include mercury from anthropogenic sources that re-volatilize after deposition. Revolatilization is an especially significant source of mercury in natural ecosystems.

Atmospheric mercury may also be emitted to the atmosphere through natural processes. Natural emissions include mercury released from: forest fires, volcanic activity, as well as evasion from oceans, fresh water, soil, vegetation and minerals.

In Wisconsin, the primary sources of atmospheric mercury emissions are coal combustion by electric utilities (and other combustion processes), medical and municipal waste incineration, and a chlor-alkali plant (the manufacture of chlorine and caustic soda).

MERCURY IN THE ATMOSPHERE

Mercury enters the atmosphere in three basic forms - as gaseous elemental mercury (Hg^0), as mercury associated with particulate matter ($Hg^{2+}_{(p)}$) in the ionic form and as reactive gaseous mercury (RGM) in the ionic form ($Hg^{2+}_{(g)}$). Most of the mercury in the air is in the elemental gaseous form. Total gaseous mercury (TGM) includes both the elemental and ionic forms (please see the definitions section). It has been estimated that 70% of TGM emissions are from human-related activities and the remaining 30% are from natural sources (2). Current research is directed at understanding the speciation of mercury in the atmosphere and the contributions of atmospheric mercury to the environment, as well as the biogeochemical cycling of the heavy metal in the environment.

Ionic forms of mercury (gaseous and particulate) are emitted into the atmosphere from both anthropogenic and natural sources. Ionic mercury is especially of interest because it is a highly reactive, water-soluble form and therefore, may easily be deposited to the environment. Research indicates that approximately 3% of total gaseous mercury is in the form of reactive gaseous mercury, and concentrations of RGM have been estimated to be on the order of 0.1 ng/m^3 (3). On an annual basis, it appears that RGM concentrations are fairly constant. However, research performed in Tennessee indicates that slightly lower levels exist during cool months as compared to warmer months. RGM has also been recognized to correlate with the meteorological variables of air temperature and solar radiation as well as with SO_2 and O_3. The reactivity of RGM likely allows this ionic form to play a strong role in atmospheric removal processes i.e., wet and dry deposition, and contribute significant mercury to the terrestrial and aquatic environments.

Ionic mercury associated with particulate matter is also an environmental concern. It is thought that particulate-phase mercury may play a large role in the amount of mercury in the various environmental compartments. $Hg^{2+}_{(p)}$ generally comprises less than 5% of total atmospheric mercury (4). It has been found that $Hg^{2+}_{(p)}$ shows trends in seasonality. Research performed by a University of Michigan team indicates that higher concentrations are generally found in the winter months. There is evidence that the primary species is $HgCl_2$. It was also learned that particle size distribution of $Hg^{2+}_{(p)}$ is bimodal, which means that $Hg^{2+}_{(p)}$ may be associated with either fine or coarse particles.

MERCURY THE POLLUTANT

Concern over the presence of mercury in the environment stems from a series of factors: (1) in some forms mercury is very volatile and hence is easily dispersed even to remote areas; (2) conversion of soluble inorganic mercury to methylmercury occurs in lake sediments and this form of mercury is readily assimilated into

biological systems by ingestion and absorption through respiratory tissue or even unbroken skin; and (3), mercury is a toxic metal that readily biomagnifies and can have significant impacts on humans. As mercury is passed through the food web, it bioaccumulates -- leading to greater and greater mercury burdens at each successive trophic level. The combination of these factors results in a significant environmental problem.

Mercury Toxicology

Mercury has known toxicological effects on human health. It may be absorbed through the respiratory tract, intestinal tract and the skin. The heavy metal passes through the lungs and enters the bloodstream when inhaled. In the bloodstream, mercury is oxidized in red blood cells and transported throughout the body.

The toxicological effects of mercury are derived primarily from its affinity for sulfhydryl groups. Bound mercury acts as a barrier to the active sites of enzymes containing sulfhydryl groups and arrests enzymatic function.

The effects of mercury depend on whether exposure is acute or chronic. Acute exposure may lead to lung irritation, coughing, shortness of breath and fever. Pulmonary edema (fluid in the lungs) may eventually develop, possibly leading to death. Chronic exposure to mercury may lead to a large number of toxicological effects. A few of the chronic effects include: spontaneous abortion, kidney damage, tremors, brain damage and liver damage, just to name a few.

Mercury may persist in the body for long periods of time. It has few excretory routes and is lipophilic. In the body, approximately half of the mercury is stored in the kidneys and the rest is distributed among the spleen, blood, liver, bones and fat tissue (5).

MERCURY IN WISCONSIN

Wisconsin's waterways include approximately 15,000 lakes, numerous rivers, and shorelines on both Lake Superior and Lake Michigan (6). Wisconsin places great importance on water quality and the effects of pollutants on aquatic biota. Approximately 3,500 of Wisconsin's lakes are seepage lakes where atmospheric input, rather than riverine input, is the major route for pollutants to enter the lake. The lakes then act as a point of entry for mercury to the environment.

Mercury enters aquatic systems via three routes: run off, direct emissions and atmospheric deposition. In the lakes, aquatic flora and fauna assimilate and bioaccumulate mercury. The accumulated mercury results in increased health concerns for humans and wildlife with fish diets. It has been found that the methylated form of mercury may "bio-concentrate more than a million-fold in the aquatic food chain" causing concern over deleterious health impacts on humans as well as wildlife (7). The consumption of mercury-laden fish by piscivorous animals has been linked to neurotoxic effects and reproductive impairment in birds and animals (8). The presence of mercury in Wisconsin's lakes, streams, and rivers has led to fish consumption advisories. Over 1000 water bodies have been sampled by the WDNR and elevated levels of mercury in fish have been found in one-third of the water bodies tested. To date, fish consumption advisories have been issued for 321 water bodies. As of yet, only 40 to 45 percent of the primary water bodies in the State of Wisconsin have been sampled (9). As sampling continues, it is expected that the list of fish consumption advisories will continue to grow, and that a statewide advisory may be conceivable in the future (9).

Economic concerns are also generated in Wisconsin where fishing related jobs are a major source of employment. An estimated 2.1 billion dollars per year in revenues are related to fishing, and 1.25 million fishing licenses are sold annually by the State of which 0.25 million are non-resident (10). Thus, mercury in the environment may have definite economic impacts if the trend continues.

The NADP network

In the 1980s, the Wisconsin Department of Natural Resources (WDNR) began to set up a network of sites under the National Atmospheric Deposition Program (NADP) to measure the atmospheric deposition of acidic compounds. At about the same time, interest was developing in quantifying the mercury inputs to the environment. Some mercury monitoring was begun by the WDNR in 1985 at selected sites in Wisconsin. These early attempts proved unsuccessful due to limitations in both the sampling and the analysis technology available to the WDNR. Beginning in 1993, the WDNR began testing a new passive deposition sampling method based on the sampler used by the Swedish Institutet för Vatten-och-Luftvårdsforskning - (IVL). After the initial testing at a single site, a network of sites was established throughout Wisconsin. Many of the sites were collocated at preexisting NADP sites that had necessary meteorological monitoring equipment as well as trained operators.

Sample collection on Wisconsin's network began in 1994 and ended in April 1999.

MONITORING SITES

SITE LOCATION

Seven sampling locations comprise the Wisconsin Mercury Deposition Network (WMDN) (see Appendix 1). The sites shown in Figure 1a run from the northwest corner of the state to the southeast. Brule River is the northwestern most site and is located on the Lake Superior shoreline. Lake Geneva, located in the southeast, is the closest to urban and industrial sources. Wildcat Mountain and Trout Lake are the most isolated sites. Five of the seven sites were originally established as NADP sites, and two sites were established as part of special projects. An important goal in site selection was to include a broad geographic distribution of sites that included remote and near-urban sites. Sites selected were considered to be isolated from locally re-entrained dust that would not be representative of true dry deposition.

SITE EQUIPMENT

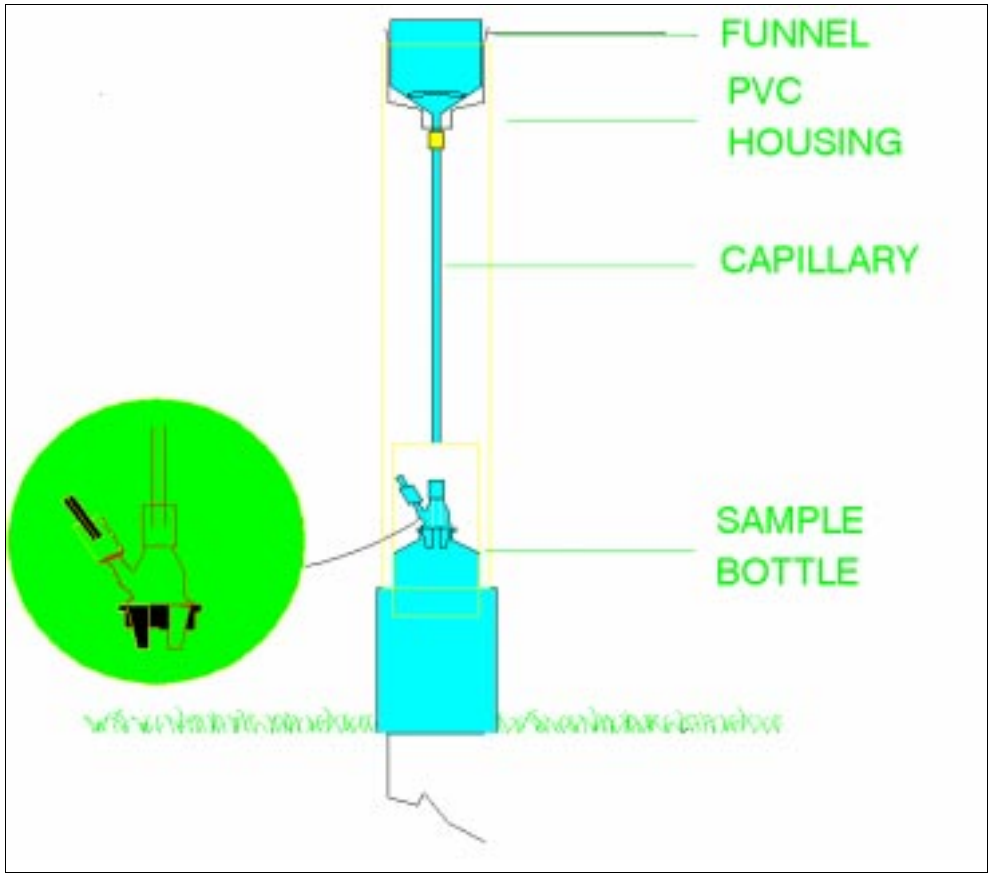
All monitoring sites were equipped with one or more passive samplers and automated Belfort rain gauges.

PASSIVE SAMPLER

The Wisconsin version of the IVL passive sampler, hereafter called the WIVL, consists of an all-glass sampling train enclosed in a support structure (Fig. 1b). The original supports were PVC piping described in Reference 1. Problems coping with Wisconsin's harsh winter environment prompted the development of an enhanced sampler with a new housing described in the Wisconsin Enhanced Passive Sampler section of this report.

The mercury data used in the production of this report was obtained using a bulk mercury sampler based on a design used by the Swedish Environmental Protection Agency (IVL). The passive sampler is designed to capture both wetfall and dryfall mercury. The sampler is designated as a "modified" bulk sampler because an inverted watch glass in the collector funnel screens out extremely large particles (objects) but smaller particles falling out (or washed out) of the atmosphere are collected along with the precipitation. Larger objects such as leaves, branches, stones, etc., are excluded along with some larger insects.

Figure 1b



Wisconsin IVL Passive Sampler Design

Smaller insects can be washed down but are mostly excluded by the watch glass, which allows the wetfall to pass through.

The WIVL's glass sampling train consists of a collecting funnel (~79 mm in diameter) with an attached 500 mm long capillary (4 mm ID). The capillary is connected to a 500 ml glass sampling bottle. The connector also has a fine capillary vent to release air from the bottle and allow rainfall to flow into the bottle (Fig 1c). The capillaries inhibit the movement of ambient air to the sampling bottle and thereby reduce mercury scavenging.

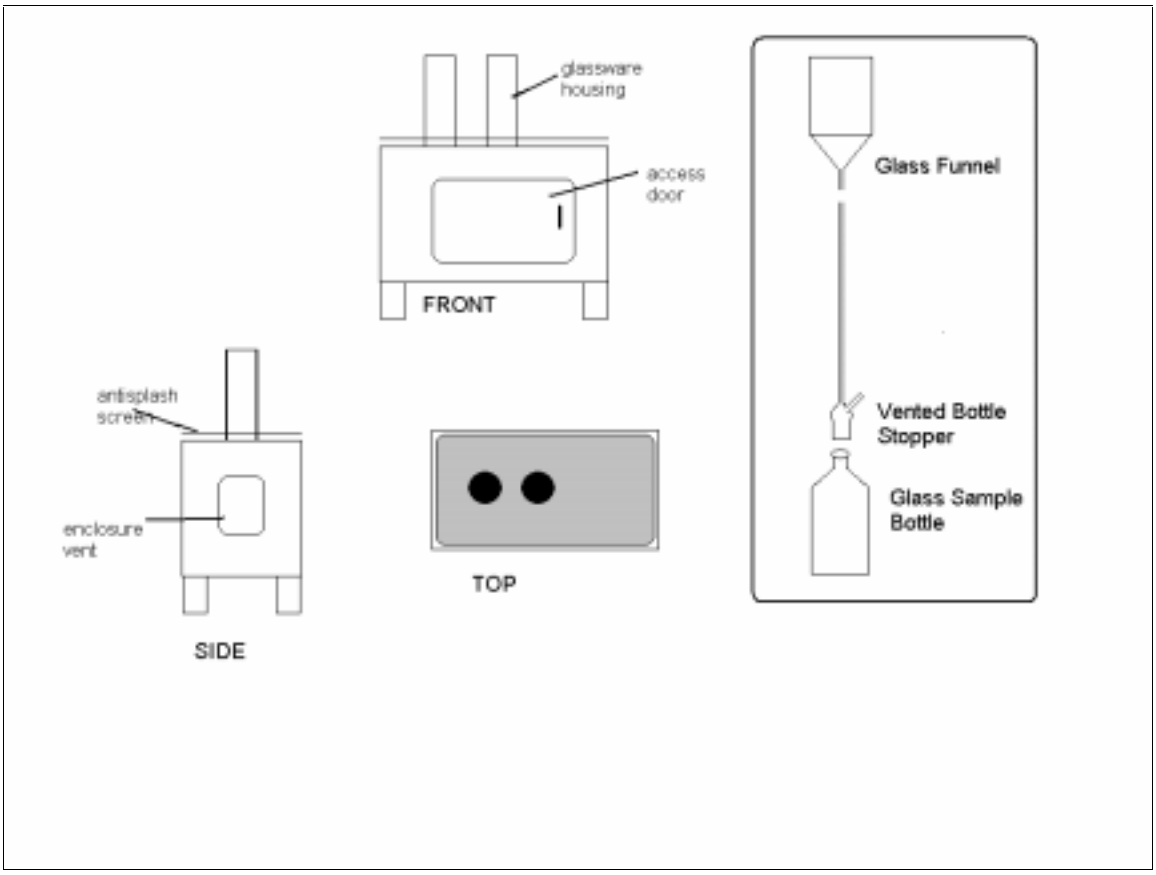
ORIGINAL IVL SAMPLING DESIGN

In the original IVL sampling design, the sampling train rests inside a PVC pipe housing that supports the glassware and excludes sunlight. The base end of the pipe is buried in the ground to maintain an upright stance. An opening in the supporting pipe allows access to the sampling bottle. A second short section of a PVC pipe, with an internal diameter approximately the same as the supporting structure's outside diameter, slides over the support to act as a cover jacket. The larger diameter pipe used for the cover jacket makes handling of the glassware easier; it allows for greater space for the 500 ml sample bottles to sit in place within the long tubular central housing and also allows heat to be more readily transferred to the funnel. The silicone rubber collar stabilizes the funnel at the top of the support pipe. The collar also excludes precipitation from entering the housing. Since all of the sites in the proposed network have access to line power, an AC heater was added to the base of the sampler (permanently installed), which provides enough heat to compensate for the wider diameter of the PVC pipe housing. This heater replaces the battery powered heating system used in the original Swedish sampler. The increased interior dimensions also provide additional space for the new type of heating system to prevent freezing during the wintertime. The heating tape is wrapped and fastened around the narrow white PVC pipe. The white PVC pipe is located inside the bottom half of the long central section of the PVC sampler housing. A thermostat on the heating tape positioned immediately below the 500 ml sample collection vessel initiates heating when the temperature inside the tube drops below 38^{o}F. Heating continues until the air temperature rises to 45^{o}F. Electric power is provided to the heater only when temperatures drop below freezing. Convection causes the warm air to rise through the sampler housing keeping the ambient temperature above freezing around the glass bottle, glass capillary, and funnel base.

WISCONSIN ENHANCED PASSIVE SAMPLER

The latest version of the WIVL sampler incorporates elements of the National Mercury Deposition Network (MDN) and the Meteorological Instrument Centre (MIC) samplers of Richmond Hill, Canada (Fig. 1c). The passive sampler was redesigned to enable easier access to the sampling glassware and to afford improved data capture during cold periods by placing a stronger heating source in the encasement. The PVC pipe housing for the sampling train has been replaced with an aluminum enclosure. The all-glass sampling train is the same as described above.

Figure 1c



Left: Wisconsin Enhanced Passive Sampler Inset: WIVL all-glass sampling train

The new sampler housing is constructed of aluminum and measures 36" (l) by 17" (w) by 18.5" (h). The box is elevated on the ground by 9" legs on each corner of the box giving the housing a final height of 27.5". Two cylinders of 4" diameter and 14.5" length rise above the top of the housing. The cylinders are insulated on the outside and the aluminum housing is insulated inside using rigid insulation panels. The primary sampling train is placed in the first tube with the second tube used for another set of glassware to test sampling precision. The top of the box is covered with an aluminum screen mounted ½" above the top, to minimize splash-back. A 15" by 20" side door makes the enhanced WIVL more easily accessible. Inside the housing, a 1000-1500 watt space heater is used to heat the enclosure and the sampling train. A thermostatically controlled 4" box fan provides ventilation for the enclosure during the warmer months. A nonmercury max./min. thermometer is located in the casement to monitor indoor/outdoor temperature.

SAMPLER OPERATION

The WIVL sampler's collection funnel is continually exposed to the atmosphere and collects a bulk precipitation sample. A bulk sample is defined as the collection of mercury from wet fall, dry fall, and occasional larger particles. These particles may include items such as dust, insects, and bird droppings. The soluble portions of an object trapped in the funnel can then be washed into the sample. The sampling train consists of a funnel, a connecting capillary and a collection bottle. The sampler relies on the long capillary to isolate the collected sample from the atmosphere. The Wisconsin system is comprised entirely of glass with a short silicon tube used for the funnel to capillary connection.

SAMPLING PROTOCOLS

The WIVL is used to collect weekly (7 day) deposition samples, with Tuesday designated as the collection day. Fresh collection bottles contain 10 ml of a 1% hydrochloric acid solution intended to act as a preservative for captured mercury. Bottles are weighed in two clean polyvinyl Zip-Loc bags before and after exposure with the sample volume determined by the difference. After removal from the sampler, the collection bottle is stoppered, stored in two Zip-Loc bags, weighed, and eventually transported to the laboratory. The site operators use the best available clean sampling and handling techniques to reduce any contamination of samples during the bottle switching operation. This includes the use of fiber-free coveralls and double gloving of the hands during sample collection. At the analysis laboratory, the samples are analyzed by USEPA Method 1631, Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (11). After analysis, the bottles are acid cleaned and the preservative added before being returned to the operators in a transport cooler. The transport cooler is used for bottle storage at the site.

The monitoring sites have additional equipment depending on the purpose of the site. Additional site equipment may include:

Belfort rain gauges, ozone analyzers, wet deposition collector, wind speed/wind direction monitoring equipment, solar radiation, and particulate monitoring equipment.

ANALYSIS LABORATORIES

Four laboratories provided the mercury analysis for data in this report. These laboratories provided data as the Department transitioned to analysis by its in-house laboratory, the Wisconsin State Laboratory of Hygiene (SLOH). Brooks Rand Laboratories of Seattle, Washington analyzed the previously reported 1994 data. In July of 1995, Frontier Geosciences of Seattle, Washington was contracted to provide a limited number of analyses while the sample analysis transitioned to the SLOH. In October of 1995, analysis started at the SLOH. By January of 1996 the SLOH had become the primary analysis laboratory for the study. During the transition to analysis at the SLOH, the University Of Wisconsin Limnology Laboratory located at Trout Lake provided analysis of split samples. The Limnology Laboratory initially provided mercury analysis for all sites. This was later reduced to routine split samples at only the Trout Lake site.

All laboratories followed the scope of work outlined in RFP "Mercury Deposition Monitoring in Wisconsin 1994 Field Study" June 21, 1994. This scope of work requires analysis outlined by Bloom and Crecelius. The method would later be the basis for USEPA Method 1631, Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence (11).

SAMPLER PERFORMANCE

We examined the sampler performance in terms of four parameters. The parameters include blanks, capture efficiency, sampling precision and the carry-over of mercury.

BLANKS

Trip blanks examined by Kolinski in 1994 were found to be below the detection levels of the analytical method. Another blank of interest was the sample in collection bottles with no measurable amount of precipitation. For our analysis, no measurable precipitation was set at less than 0.05" (0.127 cm) of precipitation. The results of the analysis are shown in Appendix 2a. The summarized results are provided for the entire network and the Trout Lake site as a specific example. In 1996 and 1997, samples with little precipitation showed measurable mercury concentrations. We examined the 1996 Trout Lake data reported on the national MDN network's web site and found there were fewer samples with small amounts of precipitation. Two samples with less than 0.05 in precipitation were reported by MDN in 1996 and these samples had a mean mercury concentration of 26.52 ng/L. The WIVL, a bulk-sampler, collects many more samples with recorded low precipitation values and these samples can be averaged for measurable mercury concentrations. This level of mercury suggests a possible background concentration for these samplers. The source of the background has not been determined and is beyond the scope of the data that we have collected to date. Possible explanations for this background phenomenon include the following. (1) Dry deposition is responsible for the background and a detectable concentration has been measured. (2) The sampler is failing to completely isolate the collection bottle from the atmosphere. (3) Atmospheric mercury is scavenged from air during sample bottle switching or during storage. (4) Mercury is leached from the glass collection bottle.

CAPTURE EFFICIENCY

The WIVL can be more efficient at sample collection since it does not rely on a moving lid to shield the sampler from dry deposition. The small opening of the sampler funnel (7.9 cm) and concerns about evaporation raised questions of capture efficiency (C.E.). Sample C.E. is determined by comparing the weight of the sample captured to the amount of precipitation measured by the Belfort rain gauge. WIVL capture efficiency is generally good. During large precipitation events, however, the WIVL captures more precipitation than the Belfort rain gauge and the monitor therefore exceeds the predicted capture efficiency based on NADP capture efficiency requirements (13). The sample weight is routinely used as a check of sample integrity, and capture efficiency has been checked since the initial testing of the sampler. Please see reference (14) for more information.

PRECISION

During the initial testing of the passive sampler, multiple samples were collected and good precision was reported (1). Multiple sampling was continued when the network was first deployed. In reporting on the 1994 data, Kolinski suggested that multiple sampling should not be continued. This suggestion was implemented in 1995 resulting in the loss of one data quality check but also facilitated sample collection by reducing the number of samples to process. Duplicate sampling continued at all sites in 1996 and at Trout Lake in 1997 as part of an inter-laboratory study. Collection precision, calculated as the percent difference, is summarized in Appendix 2b and shows good agreement between weights collected by duplicate sampling trains.

CARRY-OVER

Carry-over is defined as pollutant that remains in the sampler from the first sample and is retained until the next sample. The importance of carry-over is that the first sample is incomplete and the second sample is therefore contaminated by the previous sample. Samples may be averaged but there is a loss of time resolution leading to inaccurate estimates of mercury deposition.

The first and most visible type of carry-over occurs when samples of snow or frozen rainfall fail to pass through the funnel into the sample bottle. A major reason for redesigning the sample housing was sample freezing.

A second less obvious form of carry-over is the pollutant trapped on the glassware surface of a sampling train and carried over into the next sample. Sampling train funnels and capillary glassware were replaced periodically. Our examination of the glassware between samples showed that there was no trend of accumulation between glassware exchanges.

During past empirical examinations for carry-over, it was shown that samples following a high mercury sample are not empirically different from samples before the high event. It was also demonstrated that there is no trend indicating carry-over of samples between glassware exchanges (14).

Carry-over can also occur when dry deposition collects during a period with little rainfall and is then washed into the sample during a precipitation event in the next one-week period. This has not been examined but should not significantly affect long term averages (quarterly or average concentrations).

NETWORK PERFORMANCE

We examined the network performance in terms of three parameters. The parameters include completion, inter-laboratory testing, and comparison with another network. In this case, the comparison is with the MDN network.

DATA COMPLETENESS

The monitoring plan design calls for weekly sampling, and a total of 52 samples are expected at each site each year. The percentage of actual samples collected is summarized in Appendix 3a. The most frequent reason for sample loss was frozen samples. This occurs during extremely cold weather when the sample collected in a funnel fails to melt and travel to the collection bottle. It may also occur when a frozen capillary tube blocks samples from entering the collection bottle. The electrical heaters used in the PVC pipe enclosures were redesigned to increase data completeness but still failed to create the necessary heat to melt samples during extreme cold. This phenomenon was particularly evident at the northernmost site Brule River, located on the Lake Superior shoreline. The enhanced enclosure design deployed in 1997 appears to provide better performance. This is evident by increased sample collection in the last two quarters of 1997.

INTER-LABORATORY

While triplicate sampling was discontinued in 1995, duplicate sampling was continued. During a transition of the mercury analysis to our in-house laboratory, duplicate samples were split with the laboratory at the University of Wisconsin Limnology Center located at Trout Lake. The Limnology Center's laboratory had assisted the WDNR in the initial testing of the WIVL sampler. The results of the duplicate sampling are summarized in Appendix 3b Paired sample results, compared by relative percent difference (RPD), show a mean of 45.4% in 1996. This difference results in a significantly higher mean from the State Laboratory of Hygiene. Duplicate samples were reduced to a single site in 1997 and continues at Trout Lake to the present. The results show improvement in the 1997 samples where mean RPD is 22.5%, and the mean mercury is comparable at both laboratories.

INTER-NETWORK COMPARISON

The WDNR operates four MDN sites. Three of the MDN sites, Brule River, Trout Lake and Lake Geneva are collocated with WIVL sites. We chose to look at results from the Trout Lake site for 1996. Data for the site is available from the MDN web site and the WIVL data set for Trout Lake is larger than for Brule River. The Lake Geneva MDN site began operations in 1997 and no data is yet available. The results of the comparison are reported in Appendix 3c. The data suggests that the WIVL and MDN sampler mean mercury concentrations and mean mercury deposition values do not differ significantly. Examination of individual points does show a significant difference that does not appear in the means. While data from the WIVL and the MDN sampler are not identical, the comparison does show that the Wisconsin network is generating comparable data.

WIVL NETWORK MERCURY SUMMARY

Contents: Deposition, concentration, and seasonality of atmospheric mercury in Wisconsin's environment as measured by the Wisconsin IVL bulk mercury monitor are considered in the data analysis section of this report.

Data Completeness for Analysis

Each WIVL monitor has two sampling columns, the A-sampling train and B-sampling train as noted in the site equipment sampler description. In accordance with EPA data requirements, only those sampling trains with $\geq$75% annual data completeness i.e., $\geq$39 of 52 weeks of samples, are considered in the statistical data analysis. In addition, only those samples with $\geq$75% annual data completeness are graphically displayed. Basic statistics for all data, regardless of their level of completeness, are published in (Appendices 4a-4c).

In 1995 three sampling columns, the A-, B- and, C-sample columns, operated at each of the seven sites. Due to the extreme lack of credible data from C-columns, only the A- and B-columns were considered for the data analysis. There was a total of 14 functional sampling columns in the state. Seven of the fourteen sampling trains, or 50%, met the criterion of $\geq$75% annual data completeness. In 1996, only the A- and B-columns were in operation at the seven sites. Five of eight sites (62.5%) met the data completeness requirements in 1996. In 1997, however, the Wisconsin Enhanced Passive Sampler was installed at all seven sites and only the A-column was used to collect samples. It was decided that good inter-laboratory precision agreement exists and the additional cost did not warrant the use of the second sampling train. The exception occurred at TRL, where duplicate samples are collected weekly for the purpose of monitoring precision. The B-sampling train continues to operate at the Trout Lake site to enable inter-lab comparisons between the State Laboratory of Hygiene and the Trout Lake laboratory. Seven of eight sampling trains (87.5%) met the data criterion in 1997 with Brule River being the exception.

Climate and geography played a significant role in data completeness. A majority of the sites that met the data criterion are located in the southern portion of the state, especially in 1995 and 1996. This is principally due to warmer winter temperatures in southern Wisconsin during the winter. In 1997, we see data collection improvements due to the improved monitor design and better heating units in the monitor. Neither of the sampling trains in the Brule River monitor located in northwestern Wisconsin met the data capture criterion.

Possible Reasons for not Meeting Data Completion Goals

Reasons for not meeting data completion goals include sample freezing, broken glassware, and accidental contamination. Improvements such as better heaters and improved insulation were made to increase data completion.

As noted in the previous section, the most prevalent problem encountered was freezing of precipitation in the sampling train during cold winter months. During the 1995 sampling year, AC-powered heating tape inside the tubular PVC samplers supplied heat to the unit to help prevent sample freezing, and in the redesigned samplers of 1997, modular space heating units were placed within the sampling boxes. Although heating units were always used in the winter months, as described in the Passive Sampler section, during the coldest periods insufficient heat was produced to prevent samples from freezing. Freezing was primarily a problem in the northern part of Wisconsin.

The glassware used in the sampling train is fragile. Occasionally, a piece of glassware was broken during the sample collection process or during severe weather events. If this occurred, the sample for that week was voided and new glassware installed.

At times, accidental contamination occurred during sample collection or sample transportation. If this happened, the cause was noted and the sample voided.

MERCURY DEPOSITION

The deposition of mercury is calculated from the weekly concentration and precipitation values monitored at each site and is reported as the mass of mercury deposited to a unit area. Please see the Definition Section for a technical definition.

Total Deposition

Total deposition is the sum of all the weekly deposition values over an entire year, and it is measured in $\mu g/m^2$. The total deposition value gives the mass of atmospheric mercury per square meter that is deposited to the earth at a site over the course of a year. In this report, total deposition is calculated for each individual monitoring site.

When considering only those sampling trains that meet the data completeness criterion, the following has been observed. The range between the minimum and maximum total deposition values is relatively small during each of the years 1995-1997 (Fig 2a). Over the entire 3-year period, the range is 9.84 $\mu g/m^2$. A majority of the total deposition values lie between the 8 and 14 $\mu g/m^2$/yr. Approximately 32% are less than 8 $\mu g/m^2$/yr. Based on the A-column, it appears that the greatest amount of deposition occurred in 1996 at most sites.

In 1995, the range is very small 3.9 ug/m^2 (Fig 2b). The minimum total deposition value is 9.2 ug/m^2 (n=40), which is measured with the A-sampling train at the Wildcat Mountain State Park (WCM) site. The maximum total deposition value in 1995 is 13.1 ug/m^2 (n=42) and is also recorded at Wildcat Mountain State Park on the B-sampling train. It is unusual that both the minimum and maximum total deposition for the 1995 sampling season were measured at the same site. We note that the sample sizes are different (A-sampling train n = 40; B-sampling train n = 42), and that the values at WCM in 1995 are relatively close (9.2 ug/m^2 and 12.4 ug/m^2). This discrepancy may indicate a precision problem, a problem with the monitoring method, a problem with lab analysis or it may simply be a result of natural atmospheric differences. In general, one would expect the minimum and maximum total deposition values to be recorded at different sites as is the case in 1996 and 1997.

The minimum and maximum total deposition values in 1996 have a larger range (Fig 2c). The minimum value, 7.1 ug/m^2, is derived from the Trout Lake-B sampling train. The maximum deposition value 15.6 ug/m^2 is recorded with the A-sampling train at the Lake Geneva monitoring site. When observing the A-sampling train, the 1996 total deposition represents a more typical north-south distribution of total deposition differences in the state.

There appears to be poor agreement between A- and B-sampling trains at Suring, Wildcat Mountain, and Lake Geneva in 1996. The reasons for the discrepancies are not known.

Graph Conventions

The graphs included in the data analysis section follow specific conventions. Only those sites with > 75% data capture are depicted in graphs. The three years are represented in bar graphs by a gradation in shading. The darkest shade represents 1995, the gray shade 1996, and the white bars represent 1997. Above each bar, the sample size (total annual samples collected) is included. Along the x-axis of bar graphs, the three-letter site abbreviation and the sampling train letter is written. The y-axis indicates the amount of the measured matter whether it be mercury or precipitation. Ninety-five percent confidence intervals are also depicted in graphs. The two sampling columns (A & B) are represented by the site abbreviations with sampling train letters on the y-axis. The first set of site abbreviations represents 1995 results, the second set (or third and fourth) represents the 1996 data results, and the fifth represents the 1997 results. At Trout Lake (TRL) in 1997, there are two columns indicated by the third set of abbreviations.

Figure 2a

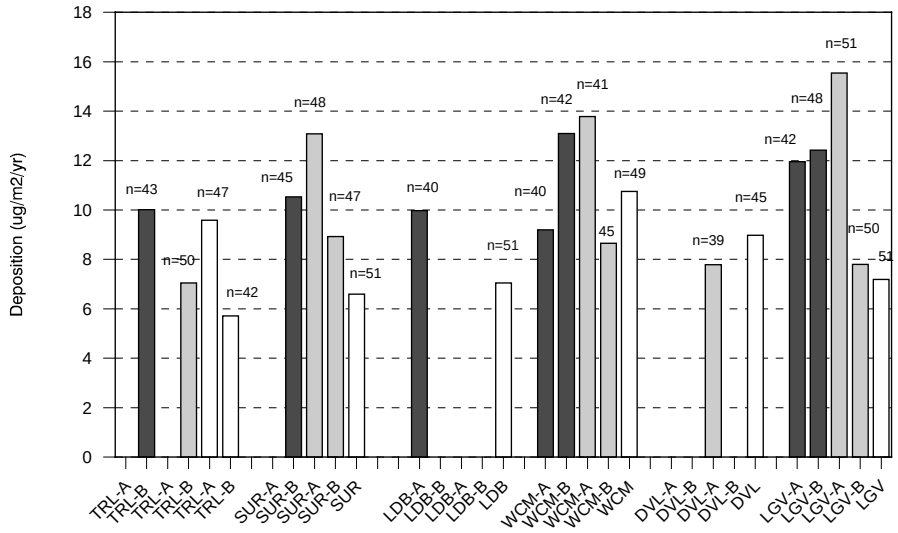


Figure 2a Total deposition ($\mu g/m^2/yr$) of atmospheric mercury during the 1995-1997 sampling period. Only those sites with ≥ 75% data capture (n ≥ 39) included. Note: The Brule River (BRU) data is not displayed in any of the following graphs. Data capture never exceeded the 75% minimum data capture criterion at BRU.

Figure 2b

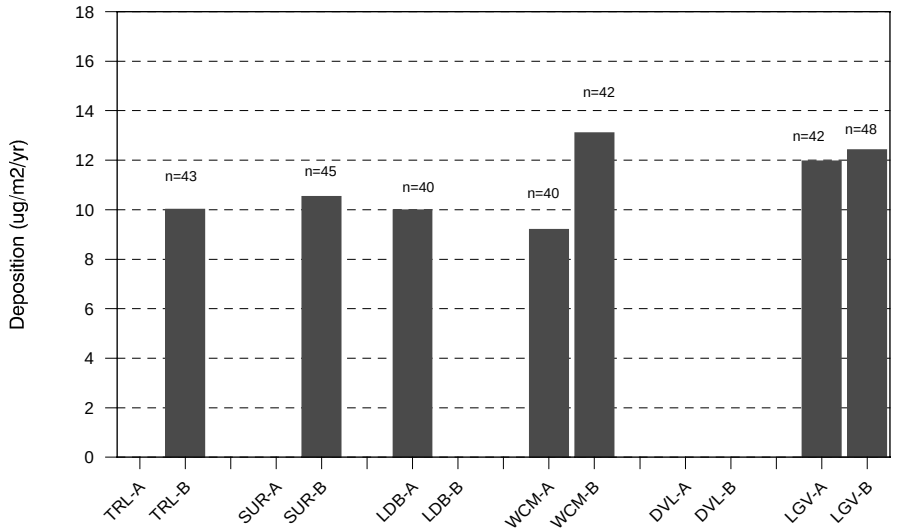


Figure 2b 1995 total deposition ($\mu g/m^2/yr$) by site. Only those sites with ≥ 75% data capture (n ≥ 39) included.

Figure 2c

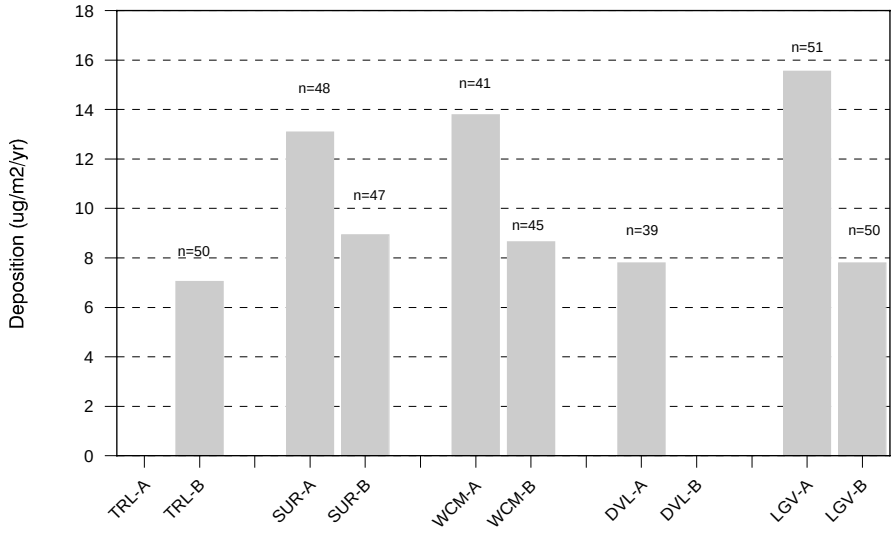


Figure 2c 1996 total deposition ($\mu g/m^2/yr$) by site. Only those sites with ≥ 75% data capture (n ≥ 39) included.

Figure 2d

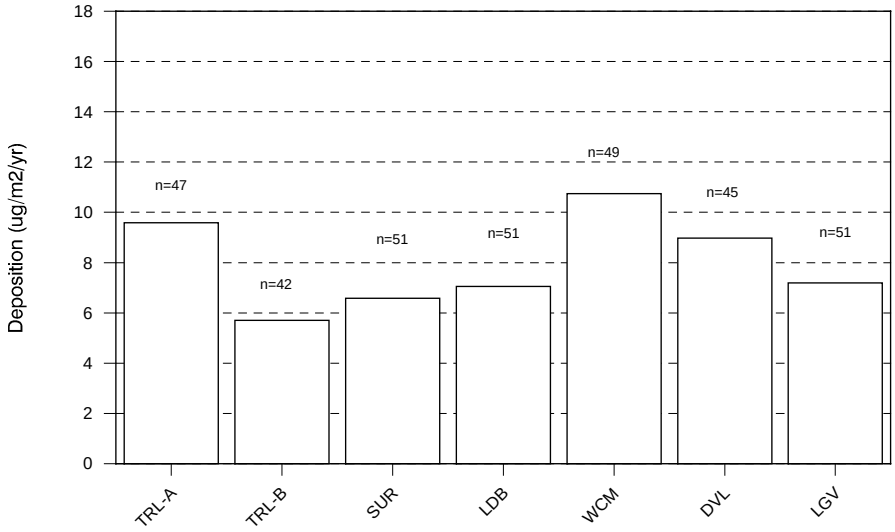


Figure 2d 1997 total deposition ($\mu g/m^2/yr$) by site. Only those sites with ≥ 75% data capture (n ≥ 39) included.

At most sites, the 1997 total deposition values appear to be lower than those in 1995 and 1996 (A-sampling train only). The range of total deposition is also smaller between the minimum and maximum during1997. The minimum value was recorded with the Trout Lake B-sampling train and is 5.7 ug/m^2 while the maximum value was recorded with Wildcat Mountain-A and is 10.8 ug/m^2 (Fig. 2d). This also represents a more typical north-south distribution of mercury deposition in Wisconsin with TRL-A being the exception.

One sample accounts for the Trout Lake A-sampling train exception. The sampling week of 6/24/97 to 7/1/97 accounts for nearly 35% of the total annual deposition for the TRL-A sampling train in that year. The concentration for TRL-A (50.8 ng/L) was five times higher than the TRL-B (10.4 ng/L) sampling train for the same one-week period. There is no legitimate reason to invalidate either concentration value.

Below is a table summarizing the maximum and minimum annual deposition within the WMDN network from 1995 to 1997. For more information on Hg deposition in the Midwest, please see references 10 through 12.

Table 1: Total Deposition Summary and Comparison

Year	Site	Total Deposition ($\mu g/m^2$)
1995	WCM-A	9.2 [1]
1995	WCM-B	13.1 [2]
1996	TRL-B	7.1 [1]
1996	LGV-A	15.6 [2]
1997	TRL-B	5.7 [1]
1997	WCM-A	10.8 [2]

[1] Indicates minimum bulk deposition value from the seven WMDN sites in the noted year.
[2] Indicates maximum bulk deposition value from the seven WMDN sites in the noted year.

The results from the A-sampling train at Wildcat Mountain State Park are interesting to consider throughout the report. Empirical evidence demonstrates that the A-sampling train at WCM consistently registers the maximum mean concentration and deposition values in the State of Wisconsin. However, this phenomenon is not statistically significant (see the following section).

Mean Weekly Deposition

The mean weekly deposition (MWD) is calculated at every site for the period 1995 to 1997. This value is obtained by averaging all of the valid weekly atmospheric mercury deposition values of a monitoring site over a one year period. A definition with an example calculation is included in the Definitions Section.

Mean weekly deposition values with 95% confidence intervals (CI) for the period 1995-1997 are depicted in Figure 3a. Annual graphs of MWD are displayed in Figures 3b-3d.

There are two points worth noting when observing the MWD graphs. The first observation is there is natural variability in the mean deposition values among sites

Figure 3a

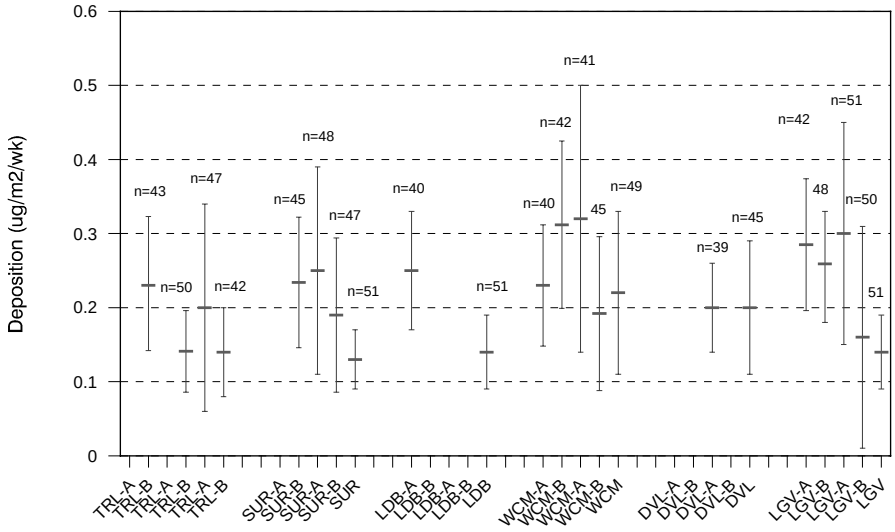


Figure 3a Mean weekly deposition (µg/m^2/wk) of atmospheric mercury with 95% confidence intervals (C.I.s) during the 1995-1997 sampling period. Only those sites with ≥ 75% data capture (n ≥ 39) included.

Figure 3b

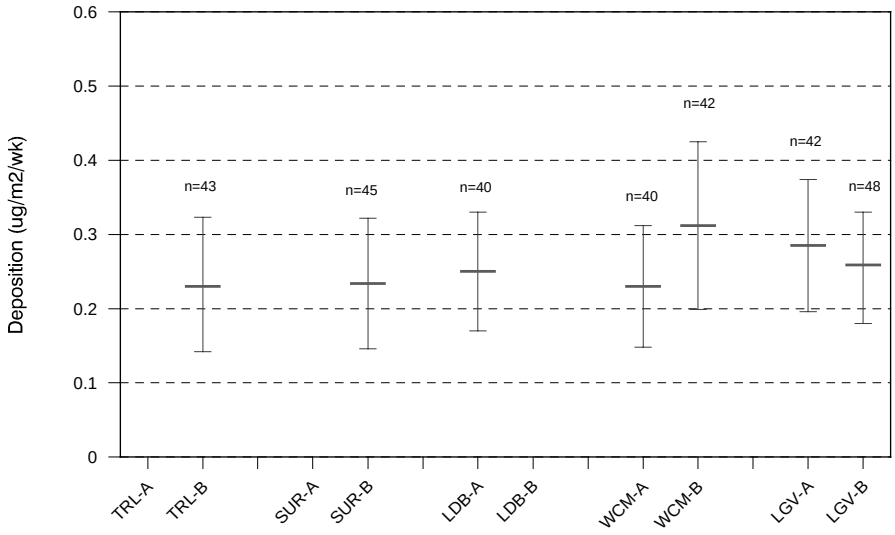


Figure 3b 1995 mean weekly deposition (µg/m^2/wk) of atmospheric mercury with 95% C.I.s by site. Only those sites with ≥ 75% data capture (n ≥ 39) included.

Figure 3c

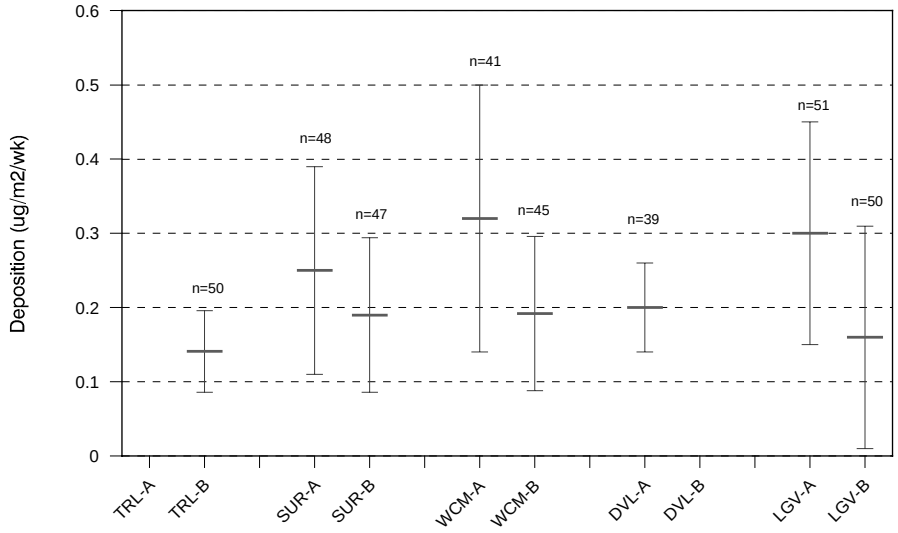


Figure 3c 1996 mean weekly deposition ($\mu g/m^2/wk$) of atmospheric mercury with 95% C.I.s by site. Only those sites with ≥ 75% data capture ($n \geq 39$) included.

Figure 3d

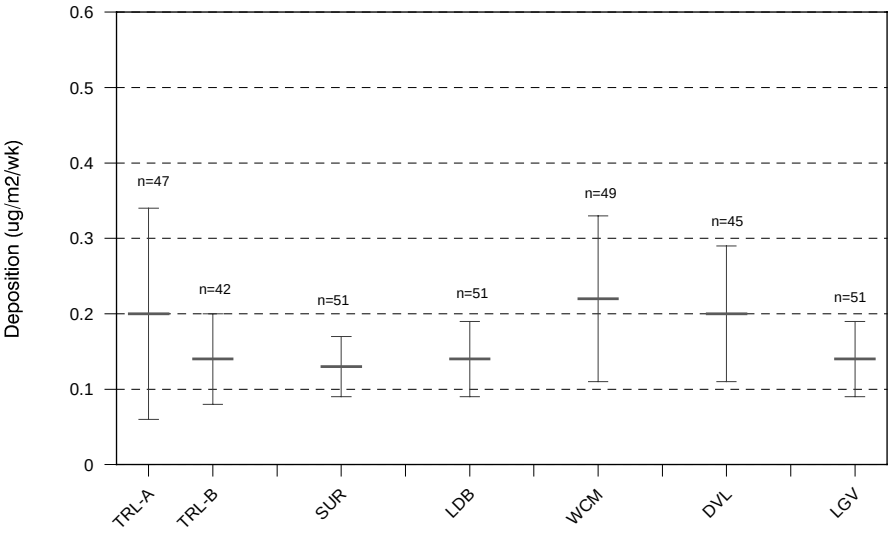


Figure 3d 1997 mean weekly deposition ($\mu g/m^2/wk$) of atmospheric mercury with 95% C.I.s by site. Only those sites with ≥ 75% data capture ($n \geq 39$) included.

within a given year (Figs 3b-3d). Empirical differences are obvious among the sites, however, based on 95% C.I.s, there are no statistically significant differences among the sites during the three year period.

There are few significant differences within sites (intra-site) during the three year period. The only statistical difference that may be of interest occurs at Lake Geneva. According to the 95% C.I., the sample result in 1997 is significantly less than A-sampling results in 1995. This indicates a decrease in the mean deposition during the three year period but is not necessarily indicative of a continuous decrease. Other statistical differences are not of significant importance.

Also worth noting is the means are generally within the 0.1 and 0.3 ug/m^2 range. Mean weekly deposition values observed with the WIVL are consistent with values found in other Midwestern states.

The statewide annual mean deposition value is also useful (please see the Definition Section). When considering only those sites with 75% data completeness or greater, the following results are yielded.

Table 2: Statewide Mean Weekly Deposition Values

Year	Sample Size	MWD with 95% CI(ug/m^2)
1995	209	0.247±0.038
1996	229	0.250 ±0.057
1997	337	0.194 ±0.064
Only those sites with ≥ 75% annual data capture included.		

This table emphasizes the inherent variability and differences of mercury deposition to the state from year to year. Please see Figure 4, a graphical depiction of the statewide mean weekly deposition with 95% C.I.s. Based on the 95% CI, there is no statistical difference among statewide means during the three year period.

Figure 4

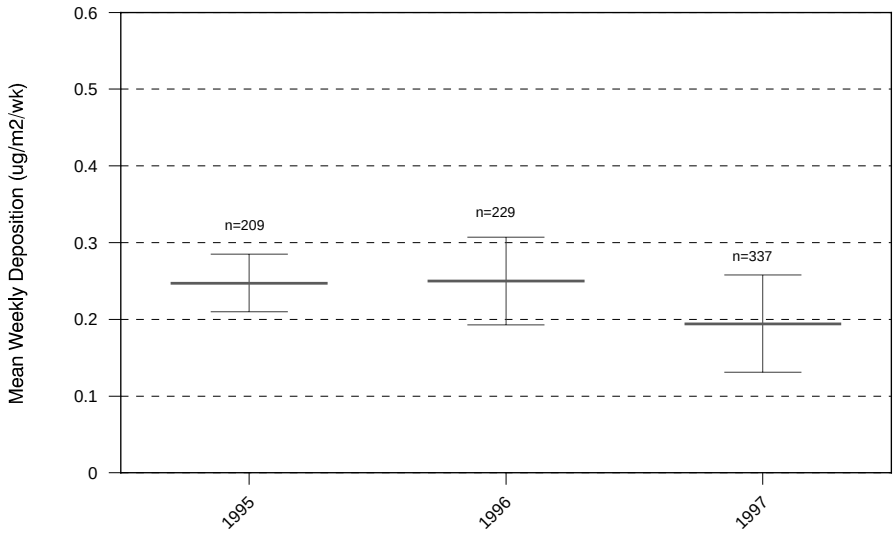


Figure 4 Statewide mean weekly deposition ($\mu g/m^2/yr$) of atmospheric mercury with 95% C.I.s by year. Only those sites with ≥ 75% data capture (n ≥ 39) included.

MERCURY CONCENTRATION

When the WDNR receives the mercury sample analysis results from the State Laboratory of Hygiene, a concentration is reported. Concentrations are given as mass per unit volume (ng/L).

Precipitation Weighted Concentration (PWC)

The precipitation weighted concentration (PWC), also known as the volume weighted concentration, is calculated for each site that meets the data capture criteria during the period 1995 to 1997. In the State of Wisconsin, 70% of the PWC means are within the 10 ng/L to 20 ng/L range (Fig 5a). These values are similar to those measured in other Midwestern and Great Lakes states. Individual years are depicted in graphs 5b – 5d.

Figure 5a

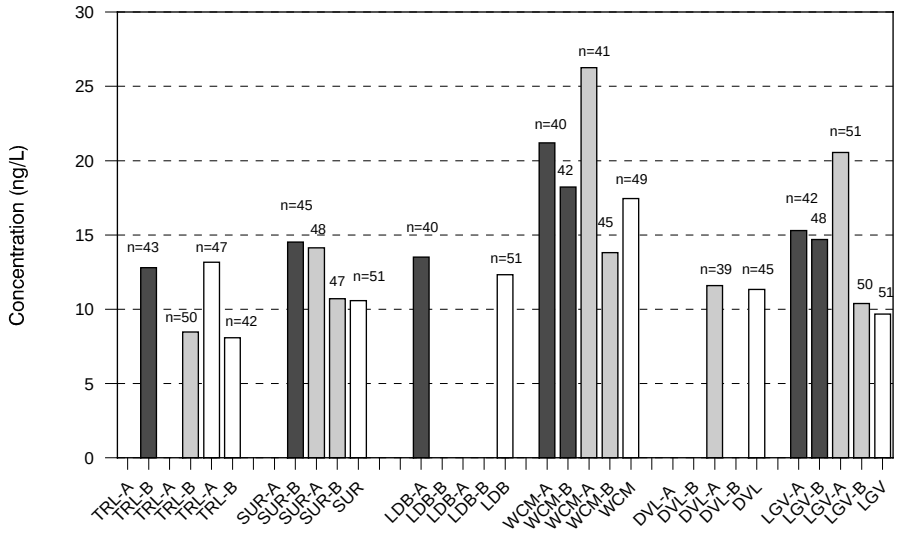


Figure 5a Precipitation weighted mercury concentration (ng/L) for the 1995-1997 sampling period. Only those sites with ≥ 75% data capture (n ≥ 39) included.

Figure 5b

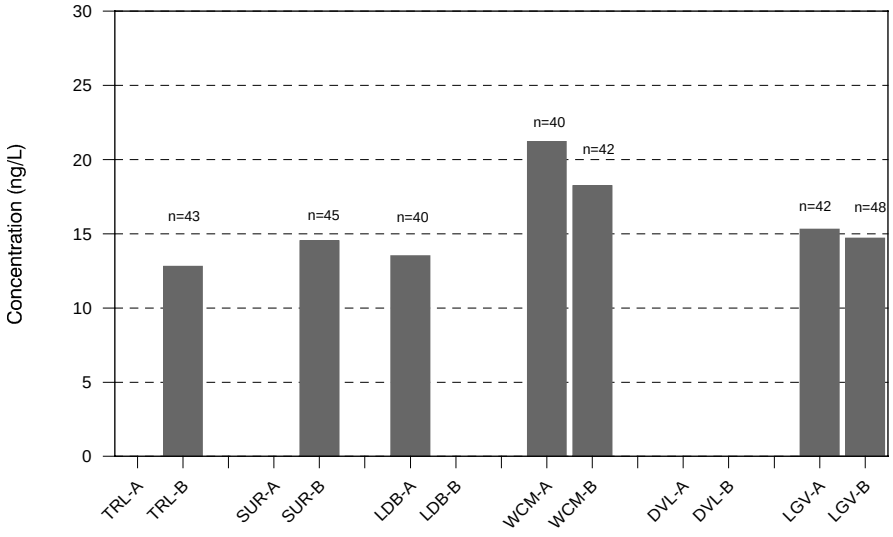


Figure 5b Precipitation weighted mercury concentration (ng/L) for 1995. Only those sites with ≥ 75% data capture (n ≥ 39) included.

Figure 5c

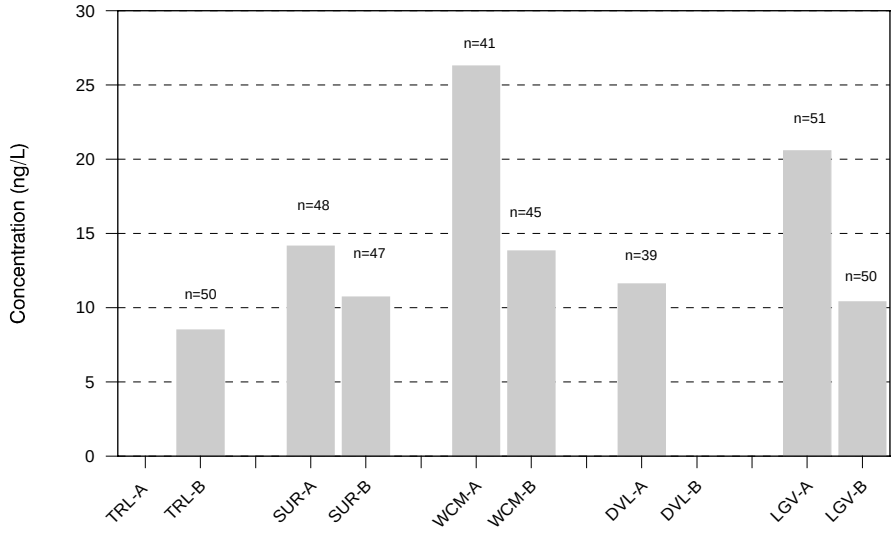


Figure 5c Precipitation weighted mercury concentration (ng/L) for 1996. Only those sites with ≥ 75% data capture (n ≥ 39) included.

Figure 5d

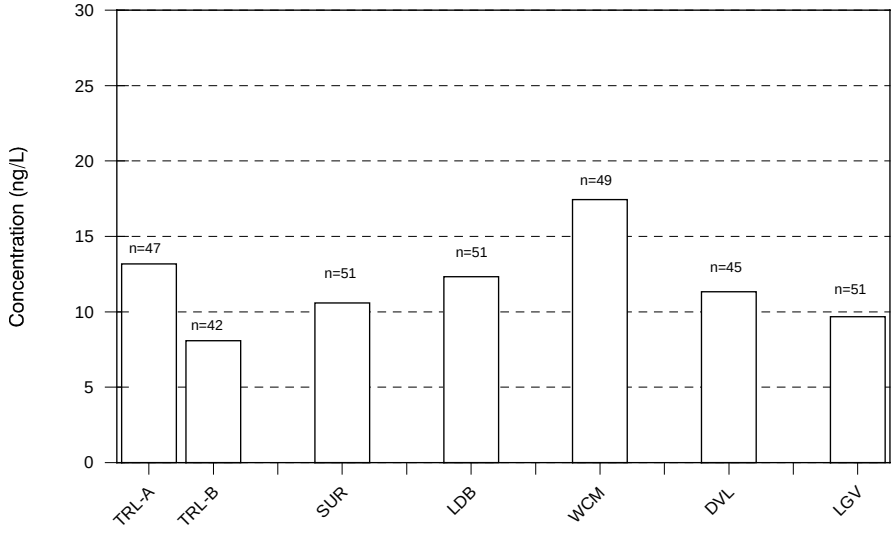


Figure 5d Precipitation weighted mercury concentration (ng/L) for 1997. Only those sites with ≥ 75% data capture (n ≥ 39) included.

The following table lists the statewide precipitation weighted mean concentrations for the three year sampling period. As a comparison with other states in the Midwest, please see references (10) and (11).

Table 3: Annual Statewide Means of Precipitation Weighted Concentrations

Year	***N*** **(# of samples)**	**Site**	**Mean PWC (ng/L) With 95% CI**
1995	7	All sites	15.75±2.7 [1]
1996	4	All sites	13.71±5.51 [1]
1997	7	All sites	11.48±2.71 [1]

[1] Statewide mean PWC

Empirically, it appears that the statewide precipitation weighted concentration mean has decreased over time. Based on an Analysis of Variance (ANOVA) test, however, there is no statistically significant difference among the years ($p = 0.22$).

A large confidence interval in 1996 exists, which is primarily due to a high precipitation weighted concentration of 26.26 ng/L at Wildcat Mountain State (Fig 6a). More long-term evidence is required to draw any conclusions about trends in precipitation weighted concentration data.

The three sites meeting data completeness criterion during the three-year sampling period were compared. It was found, based on an ANOVA, that the 3-year means between the WCM-A sampling train and TRL-B sampling train are significantly different ($p = 0.016$) with the mean at WCM being much greater than at TRL. There is no statistical difference between WCM-A and LGV-A sampling train ($p = 0.11$). This emphasizes the fact that the maximum precipitation weighted concentration during the period 1995-1997 is found at Wildcat Mountain on the A-sampling train. The monitor at Wildcat Mountain also recorded the maximum total annual deposition values in 1995 and 1997. This phenomenon requires additional study to search for a sources that may exist downwind of the monitor.

Concentration

After analysis at the Wisconsin State Laboratory of Hygiene, a weekly mercury concentration is reported to the WDNR for each valid sample. The concentration, given in ng/L, is not volume weighted, i.e., it does not take into consideration the weighting based on the amount of precipitation. As noted before, only data with $\geq$75% data completeness are considered for statistical analysis in this report.

Intra-annual Comparisons

Mean mercury concentrations with 95% confidence intervals were calculated for each sampling train at all sites during the three year period (Fig 6a-6e). (Note: Figure 6b excludes the Suring-B sampling train from 1995 due to its extremely large confidence interval.) During the three year period, for data with $\geq$75% data completeness, no statistical differences exist when intra-annual (within a given year) comparisons among the sites are made (Figs. 6c-6e). However, there are significant differences among the sites when inter-annual (between years) comparisons are performed.

1995

The mean mercury concentrations in 1995 are more variable than in 1996 and 1997 (Fig. 6b). Site means range from approximately 19 ng/L to 58 ng/L (Fig. 6c). The resultant range of 39 ng/L is large as compared to the ranges in 1996 and 1997. The average of the mean concentrations is 35.3 ng/L. There is not a statistically significant difference among the mean concentrations at the seven sites with $\geq$75% data completeness in 1995.

Although the A-sampling train at Suring does not meet the 75% data completeness criterion in 1995, empirically it is worth noting that both the A and B-sampling trains at the Suring monitoring site have high means with large confidence intervals due to suspicious concentrations on 01/31/95. During this week, the concentrations are: A-sampling train: 1094 ng/L and B-sampling train: 1109 ng/L. These concentrations are much greater than the mean noted above. The means excluding the 01/31/95 samples present for the A and B-sampling train are: 70.22 and 34.46 ng/L respectively as compared to 99 ng/L and 58 ng/L. No objective reason exists for us to invalidate the data from 01/31/95.

In general, intra-site agreement between the A-sampling train and B-sampling train concentration means is good. This can be recognized by comparing the means (Figs 6c-6e). There are some differences that may be due to unequal sample sizes (*n*). Though it is not statistically significant, it should also be noted that Wildcat Mountain State Park has relatively high mean mercury concentrations: A-sampling train: 25 ng/L and B-sampling train: 43 ng/L in 1995.

1996

In 1996, the range among the concentration means decreases substantially to 11.7 ng/L (Fig 6d). No significant difference exists among the sites with $\geq$75% data completeness. Among those sites, the maximum mean concentration is found at Wildcat Mountain which is 27.2 ng/L, while the minimum mean concentration of 15.5 ng/L occurs at Devils Lake State Park. There are lower concentrations recorded at Brule River, Trout Lake and Lake DuBay, however, these sites do not meet the data completeness criterion.

1997

In 1997, the mean mercury concentrations all lay within a very small range (Fig. 6e). The range is 3.8 ng/L. None of the concentrations is significantly different, but empirical differences exist. Again we see that Wildcat Mountain (WCM) has the highest concentration of all the sites. Though this may not be statistically significant, WCM tends to have the highest mean concentration during all three years.

It is evident that a steady decrease in the range of concentrations exists during the three year period. Possible reasons for this occurrence are: (1) improved sampling practices (including new samplers), (2) environmental factors (temperature, precipitation, etc.), and a (3) change of laboratory. No conclusions about trends are drawn in this report based on the limited size of the data set.

There are many possible reasons for differences in concentration and deposition values during the three year period. (1) Improved sampling practices may result in better and cleaner sampling collection reducing possible sample contamination. As site operators become more experienced in sample collection, the possibility of sample contamination should decrease. New samplers were installed at each monitoring site in 1997. (2)

Environmental factors such as precipitation patterns play a key role in the deposition of atmospheric mercury to the terrestrial environment. Approximately 50% of the precipitation received in Wisconsin is from convective storms occurring primarily in the spring and summer, and these storms are variable in their distribution across time and space. If precipitation is more variable in amount and intensity, the resultant mercury concentrations will also vary, and seasonal and inter-annual differences may exist. (3) In 1997, monitoring with B-sampling trains at all sites, but Trout Lake, was discontinued, and the State Laboratory of Hygiene was named the exclusive analysis laboratory for mercury samples. Greater precision in laboratory analysis may cause the small changes in mercury concentrations we see.

Inter-annual comparisons

Although no statistically significant differences exist among sites within a given year, inter-annual differences do exist. Most meaningful for this study is to compare 95% confidence intervals for a single site across the three year period. There are three sampling trains, which meet the $\geq$75% data completeness criterion for the three year period. They are: Trout Lake-B (TRL-B), Wildcat Mountain-A (WCM-A), and Lake Geneva-A (LGV-A).

Across the three year period, there are no statistically significant differences in mercury concentrations with the TRL-B sampling train. On the Wildcat Mountain A-sampling train, a statistical difference between 1995 and 1997 exists, indicating a statistically significant decrease in concentration during the three year period. There is no statistical difference on the LGV-A sampling train between the years 1995 and 1996 as well as 1995 and 1997. However there is a statistically significant decrease in concentration between 1996 and 1997. This is baseline information, and more long-term data is required to substantiate trends in the environment.

Figure 6a

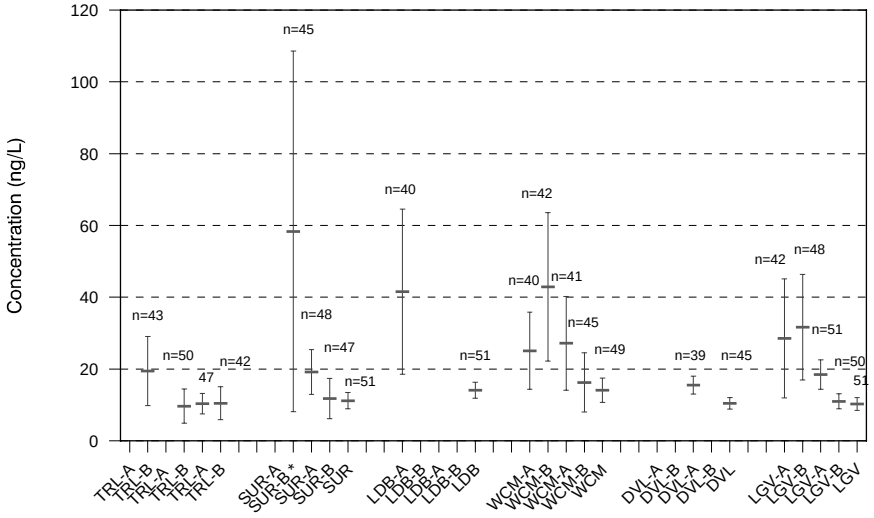


Figure 6a Mean mercury concentrations (ng/L) for the 1995-1997 sampling period. Only those sites with ≥ 75% data capture (n ≥ 39) included. * This graph includes the 1995 SUR-B data, which contains suspicious but not invalid data.

Figure 6b

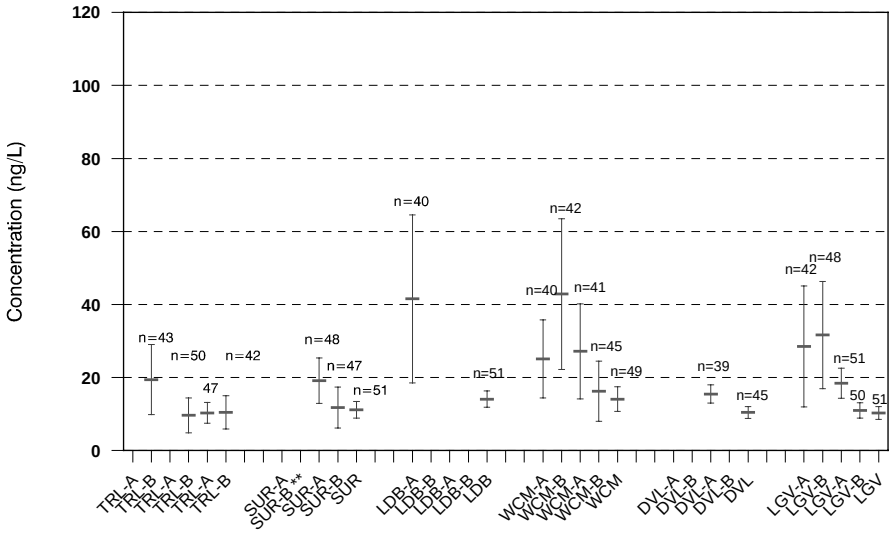


Figure 6b Mean mercury concentrations (ng/L) for the 1995-1997 sampling period. Only those sites with ≥ 75% data capture (n ≥ 39) included. This graph excludes the 1995 SUR-B data, which contains suspicious but not invalid data. This enables a better comparison among the remaining sites.

Figure 6c

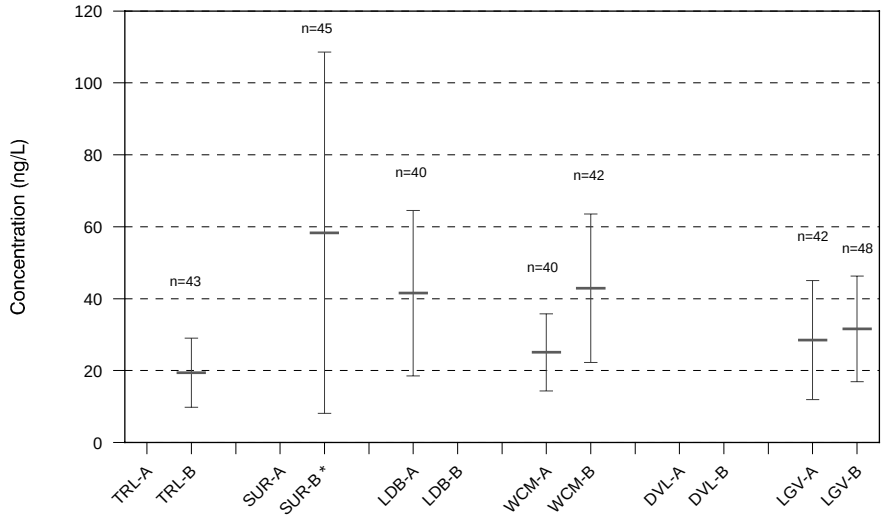


Figure 6c Mean mercury concentrations (ng/L) for the 1995. Only those sites with ≥ 75% data capture (n ≥ 39) included. * This graph includes the 1995 SUR-B data, which contains suspicious but not invalid data.

Figure 6d

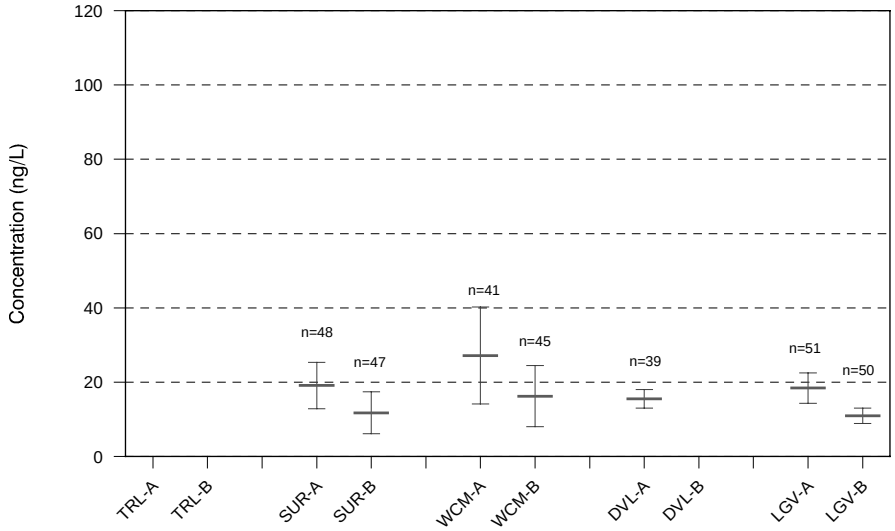


Figure 6d Mean mercury concentrations (ng/L) for the 1996. Only those sites with ≥ 75% data capture (n ≥ 39) included.

Figure 6e

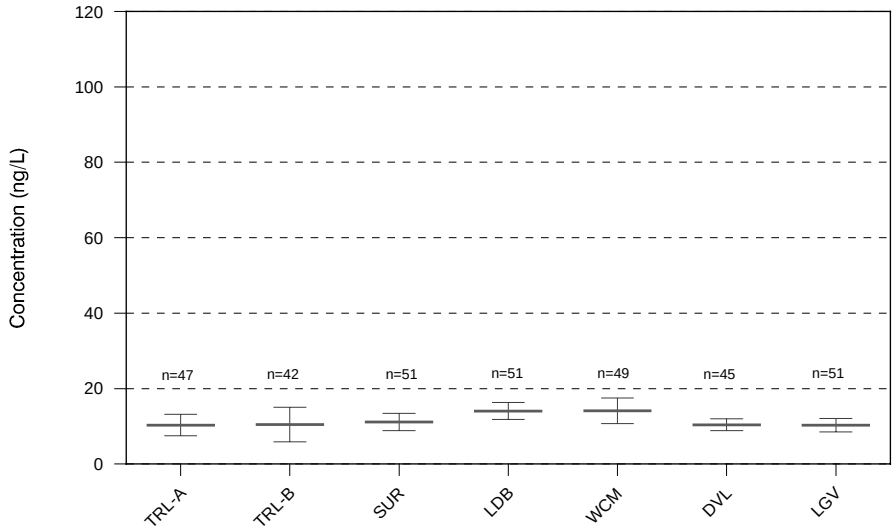


Figure 6e Mean mercury concentrations (ng/L) for the 1997. Only those sites with ≥ 75% data capture (n ≥ 39) included.

TOTAL ANNUAL PRECIPITATION

Each site in the mercury monitoring network is equipped with a Belfort rain gauge that meets EPA data collecting requirements. The rain gauge supplies the weekly total precipitation values that are converted from inches to centimeters in order to calculate the weekly deposition values. All valid precipitation samples for a 52-week period are summed at each site resulting in the total annual precipitation value.

There are existing National Weather Service (NWS) weather monitoring sites near all of the mercury monitoring sites. The NWS sites offer a 30 year mean annual precipitation value. The total annual precipitation values derived from the Belfort rain gauges located at the mercury monitoring sites are comparable to the mean annual total precipitation values obtained from the NWS meteorological monitoring sites. Most of the mercury sites have annual precipitation totals falling within the 60cm to 80cm range, while the long-term, climatological annual averages at nearby weather monitoring stations fall within the 70cm to 85cm range (Figs 7a-7d). Differences may be due to the natural variability of precipitation events or rain gauge instrumentation differences.

Figure 7a

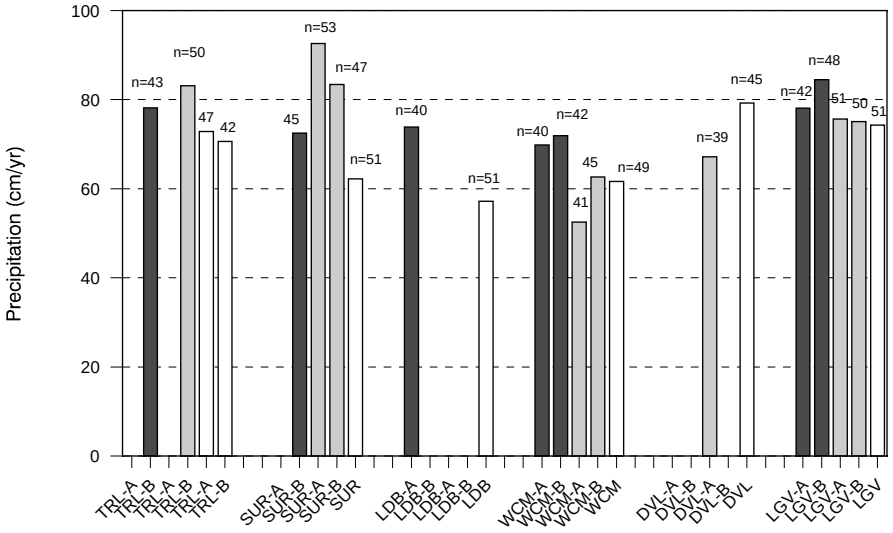


Figure 7a Total precipitation (cm/yr) for the 1995-1997 sampling period. Only those sites with ≥ 75% data capture (n ≥ 39) included.

Figure 7b

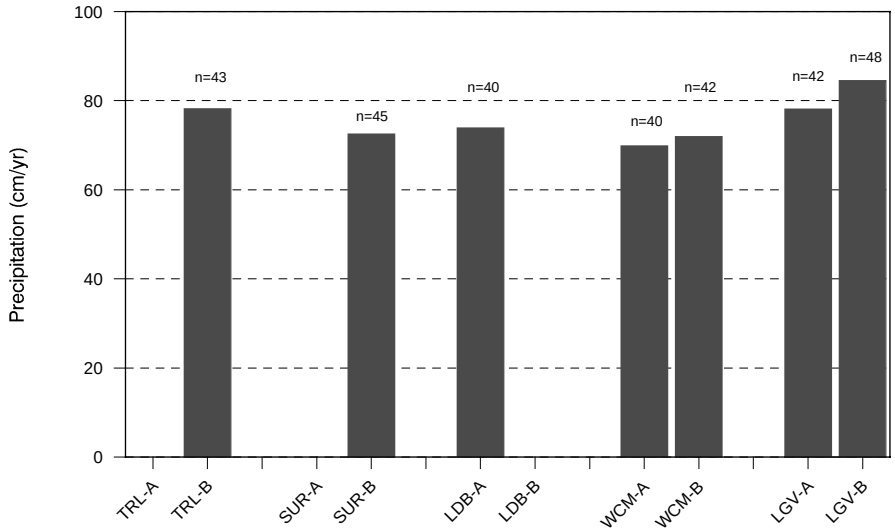


Figure 7b Total precipitation (cm/yr) for 1995. Only those sites with ≥ 75% data capture (n ≥ 39) included.

Figure 7c

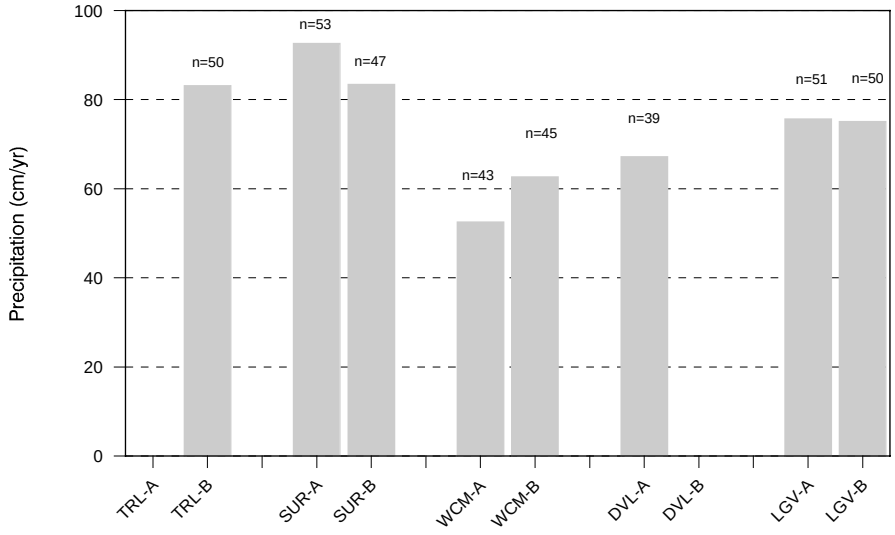


Figure 7c Total precipitation (cm/yr) for 1996. Only those sites with ≥ 75% data capture (n ≥ 39) included.

Figure 7d

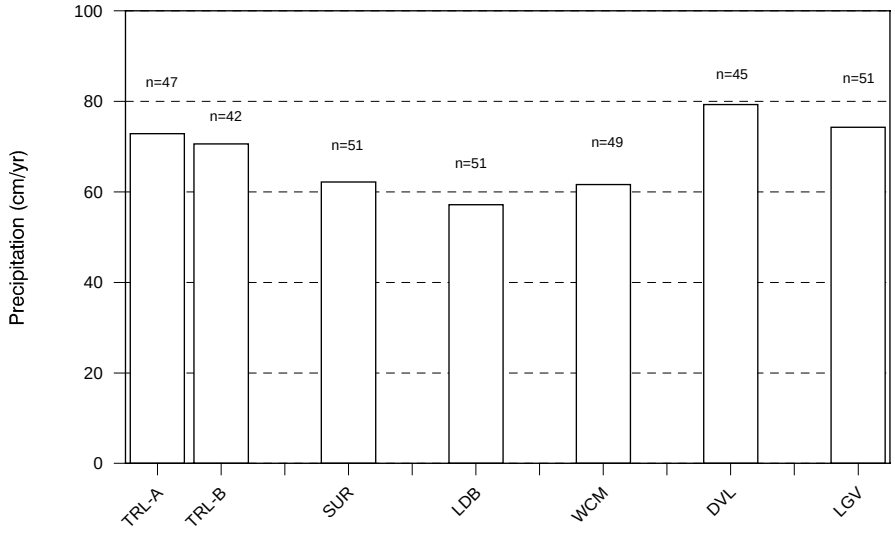


Figure 7d Total precipitation (cm/yr) for 1997. Only those sites with ≥ 75% data capture (n ≥ 39) included.

THREE SITE COMPARISON

This analysis considers data from the TRL-B, WCM-A and LGV-A sampling trains meeting the ≥75% data completeness requirement for the period 1995-1997. In addition, these sites are distributed over a large north-to-south area in the state providing a good representation of values throughout Wisconsin.

Seasonal Mercury Concentration Data

Mean mercury concentrations vary from season-to-season and year-to-year across the State of Wisconsin. The highest mean seasonal mercury concentrations are generally found during the spring season, however, there are some exceptions. The exceptions occur at WCM in 1995 and LGV in 1996 (Fig. 8a). WCM-A and LGV-A experience elevated mean seasonal concentrations during the winter (ranging from 35 to 45 ng/L) and spring (ranging from 42 to 53 ng/L) of 1995 (Fig 8b). In most cases, mean winter concentrations are below 10 ng/L, and mean spring concentrations are below 25 ng/L (Fig. 8a). Wildcat Mountain experiences a very high mean seasonal mercury concentration during the spring of 1996 (71.9 ng/L), which is due to a series of high weekly concentrations (Table 4) and (Fig. 8c).

Table 4: High Weekly Hg Concentrations at WCM (Spring 1996)

Date	Concentration (ng/L)
04/16/96	149.5
04/23/96	85.5
04/30/96	12.5
05/07/96	64
05/14/96	99.5
05/21/96	40.5
05/28/96	150
06/04/96	383

The 1997 mean seasonal mercury concentrations appear to represent more typical concentrations in the state (Fig. 8d).

Figure 8a

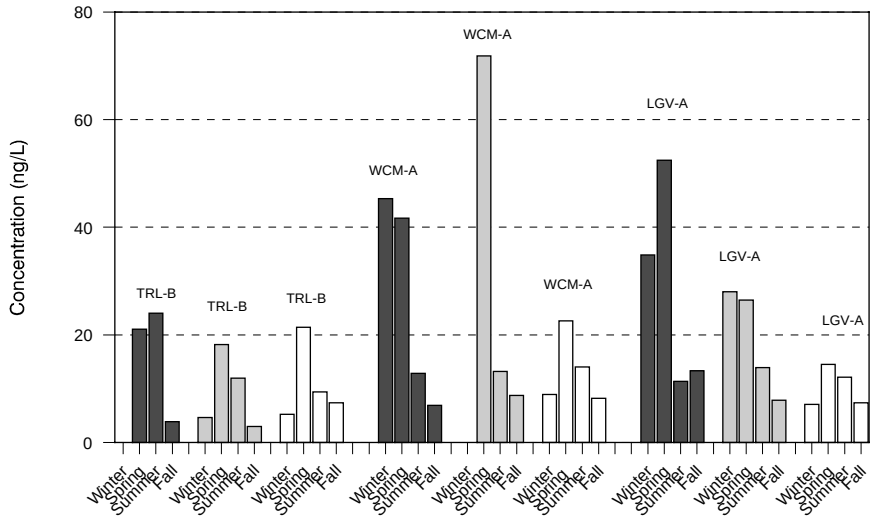


Figure 8a Seasonal mean concentrations (ng/L) for the 1995-1997 sampling period. Only those samplers with ≥ 75% data capture (n ≥ 39) for the entire three year period are included. The samplers are TRL-B, WCM-A and LGV-A.

Figure 8b

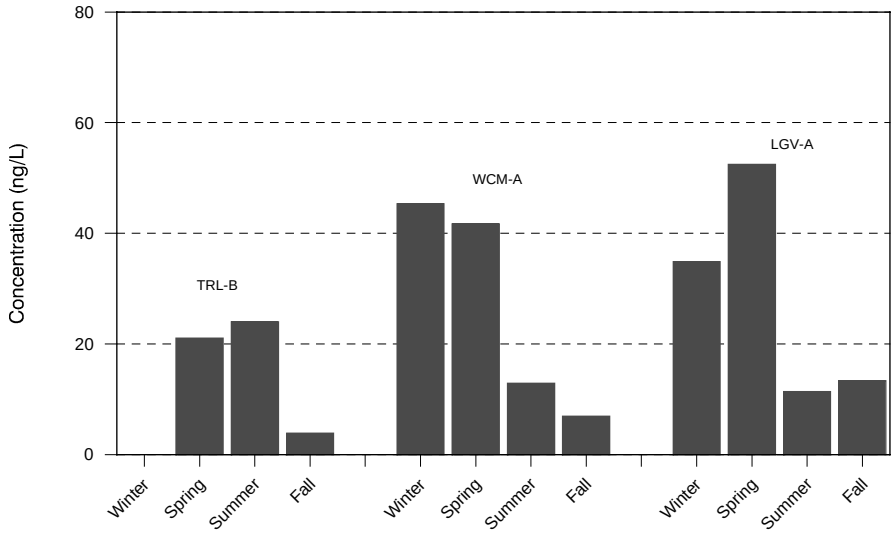


Figure 8b Seasonal mean concentrations (ng/L) for 1995. Only those samplers with ≥ 75% data capture (n ≥ 39) for the entire three year period are included.

Figure 8c

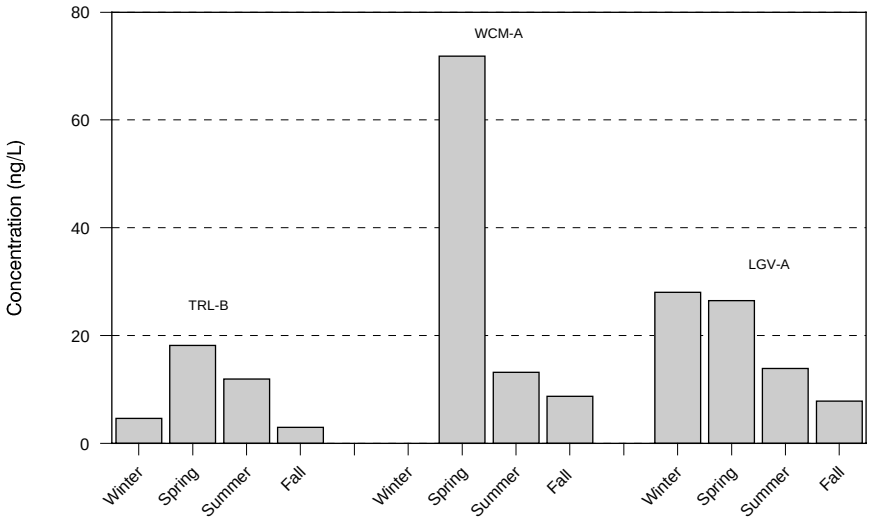


Figure 8c Seasonal mean concentrations (ng/L) for 1996. Only those samplers with ≥ 75% data capture (n ≥ 39) for the entire three year period are included.

Figure 8d

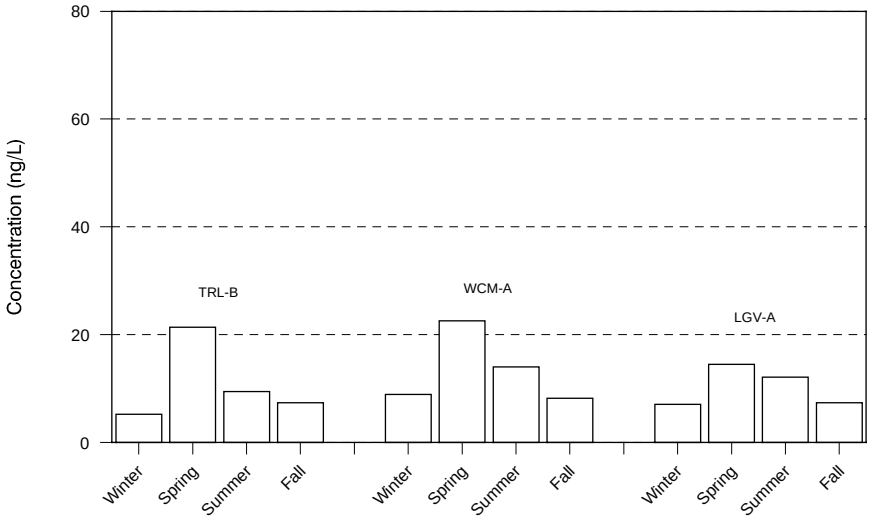


Figure 8d Seasonal mean concentrations (ng/L) for 1997. Only those sampling trains with ≥ 75% data capture (n ≥ 39) for the entire three year period are included.

Seasonal Deposition

Seasonal and annual deposition variations exist for atmospheric mercury deposition. Figures (9a-9d) depict seasonal deposition at TRL-B, WCM-A & LGV-A. Generally, seasonal deposition values are lowest in the winter and fall, and there is a marked increase in mercury deposition in the spring and summer.

Trout Lake, located in the north central portion of the state, is witness to a summertime maximum of atmospheric mercury deposition during the years 1995-1997 (Fig. 9a). Trout Lake has typical summertime deposition values within the range of 2 to 5 ug/m^2. In 1996 and 1997, less atmospheric mercury deposition occurs during each season than in 1995. Springtime mercury deposition is within 1 ug/m^2 of the summer deposition during 1996 and 1997, and winter and fall deposition values are less than 1 ug/m^2.

Wildcat Mountain, located in southwestern Wisconsin, exhibits a clear springtime maximum in atmospheric mercury deposition (Fig. 9a). Spring and summertime deposition are generally in the 3 to 5 ug/m^2 range at Wildcat Mountain, while winter and fall deposition are relatively low.

In the spring of 1996, there is a significant increase in deposition at WCM (10.8 ug/m^2). A combination of factors results in a large deposition value. There are slightly above average precipitation values as well as above-average mercury concentrations in some of the spring 1996 samples that caused the high deposition value. The following table lists the springtime weekly deposition values.

Table 5: 1996 Springtime Weekly Values at Wildcat Mountain

Date	Concentration (ng/L)	Precipitation (cm)	Weekly Hg Deposition (ug/m^2)
04/16/96	72.45	2.43	1.77
04/23/96	60.57	1.39	0.85
04/30/96	64.31	0.20	0.13
05/07/96	163.2	1.04	1.70
05/14/96	184	1.57	2.90
05/21/96	150.4	0.69	1.03
05/28/96	30.11	2.46	0.74
06/04/96	8.85	6.27	0.56

The mean weekly deposition value at Wildcat Mountain during the 1996 sampling season is 0.336 $\pm$ 0.18 ug/m^2. All but one of the spring deposition values exceed the upper bound of the 95% confidence limit, and the atmospheric mercury deposition values found at Wildcat Mountain in the spring of 1996 are all significantly greater than the mean. There is no reason to believe that the values are suspect or invalid.

Similarly, a springtime maximum in atmospheric mercury deposition occurs at Lake Geneva in southeastern Wisconsin. The deposition value (11.2 ug/m^2) reflects levels measured at WCM during the same season. This is the highest seasonal deposition value recorded at any of the three sites meeting the data completeness requirement during the three year data collection period.

Atmospheric mercury tends to increase during the spring and summer months due to a number of factors including increased precipitation and warmer temperatures. Increased precipitation amounts are associated with strong storms during the spring and summer.

Temporal and geographical differences in deposition exist within the state. Comparing three years of deposition data from the Trout Lake B-sampling train, the Lake Geneva A-sampling train, and the Wildcat Mountain A-sampling train, we see that all samplers have the spring and summer augmentation in mercury deposition (Fig. 9a). There is more deposition at Lake Geneva and Wildcat Mountain in 1996 than Trout Lake. Weekly deposition patterns at Wildcat Mountain and Lake Geneva appear to behave similarly during the entire 3-year period. This may be because they are affected by the same storm systems and are relatively similar in a climatological sense.

Figure 9a

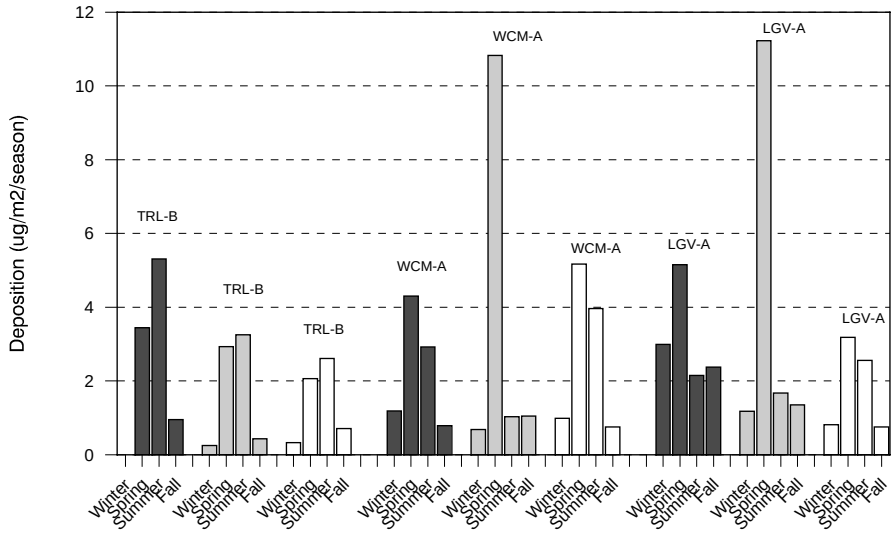


Figure 9a Seasonal mean deposition ($\mu g/m^2$) for the 1995-1997 sampling period. Only those sampling trains with ≥ 75% data capture (n ≥ 39) for the entire three year period are included. The sampling trains are TRL-B, WCM-A and LGV-A.

Figure 9b

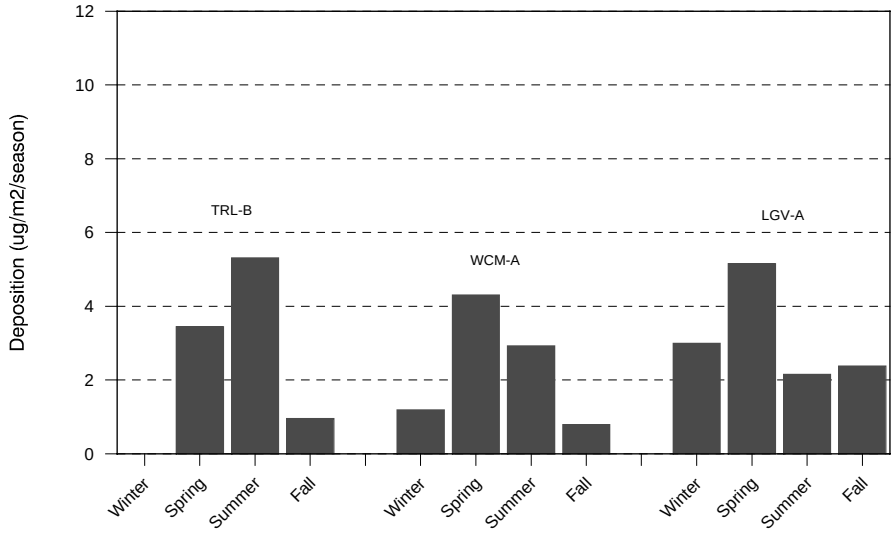


Figure 9b Seasonal mean deposition ($\mu g/m^2$) for 1995. Only those sampling trains with ≥ 75% data capture (n ≥ 39) for the entire three year period are included.

Figure 9c

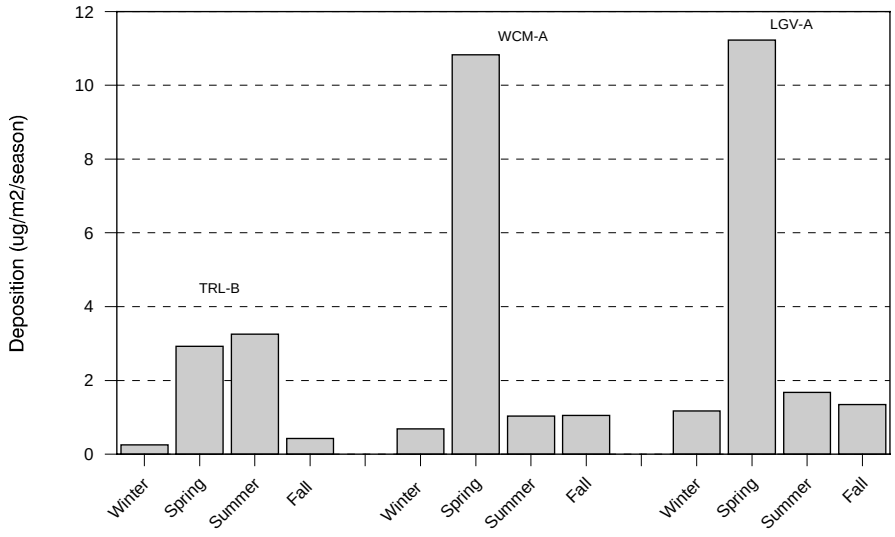


Figure 9c Seasonal mean deposition ($\mu g/m^2$) for 1996. Only those sampling trains with ≥ 75% data capture (n ≥ 39) for the entire three year period are included.

Figure 9d

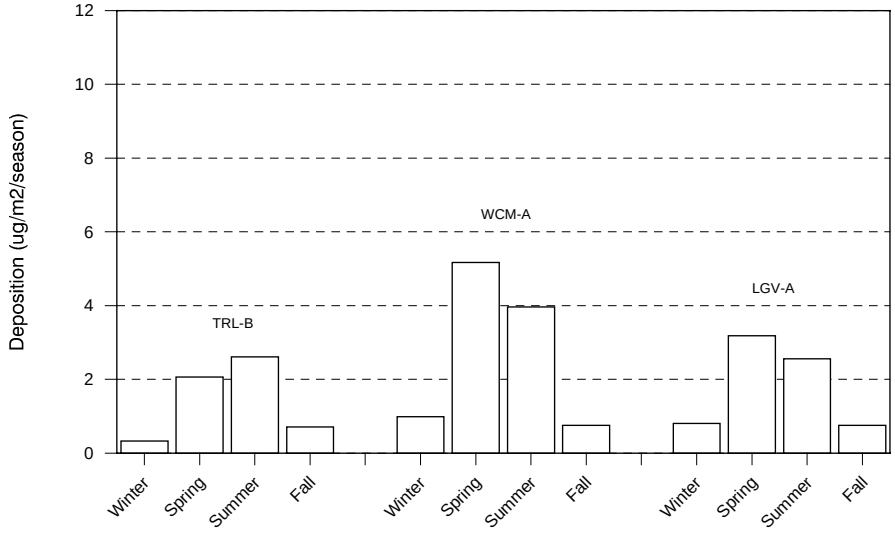


Figure 9d Seasonal mean deposition ($\mu g/m^2$) for 1997. Only those sampling trains with ≥ 75% data capture (n ≥ 39) for the entire three year period are included.

Seasonal Precipitation Weighted Concentrations

Mean seasonal precipitation weighted concentrations (PWC) also vary temporally and geographically (10a). A majority of the seasonal PWCs are below 5 ng/L, however, there are a few exceptions. In this comparison, the highest PWCs generally occur in the springtime at the southern sites (WCM & LGV) and in the summer at TRL, the northern site.

The lowest PWCs usually occur in the winter and fall, however, in 1995, the highest PWC values at Wildcat Mountain occur during the winter and fall (Fig. 10b). Non-weighted concentrations at WCM in 1995 indicate that winter and spring average concentrations are the highest (Fig. 9b), and that summer and fall concentrations are low. By volume weighting concentrations, the perceived environmental concentration results. In this case, the spring concentration is the lowest and the fall concentration is as high as the winter concentration. This demonstrates how the weighting process impacts the concentration results.

The seasonal PWCs calculated in 1996 indicate substantial springtime PWC values, both of which exceed 14 ng/L, at WCM and LGV (Fig.10c). The PWC at LGV is more environmentally significant than the mean spring concentration would indicate (Fig. 9c). Finally, in 1997 there is more similarity between PWCs and laboratory determined concentrations (Fig. 10d).

Figure 10a

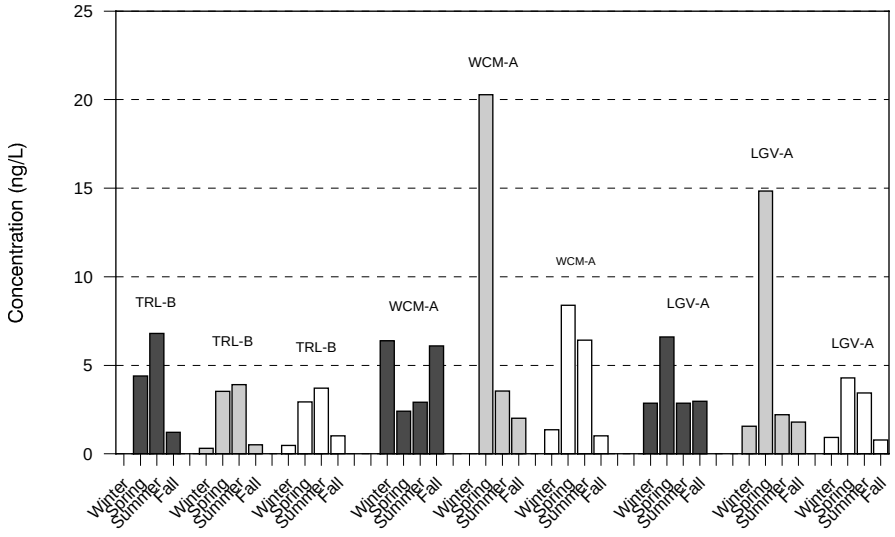


Figure 10a Seasonal precipitation weighted concentration (ng/L) for the 1995-1997 sampling period. Only those sampling trains with ≥ 75% data capture (n ≥ 39) for the entire three year period are included. The sampling trains are TRL-B, WCM-A and LGV-A.

Figure 10b

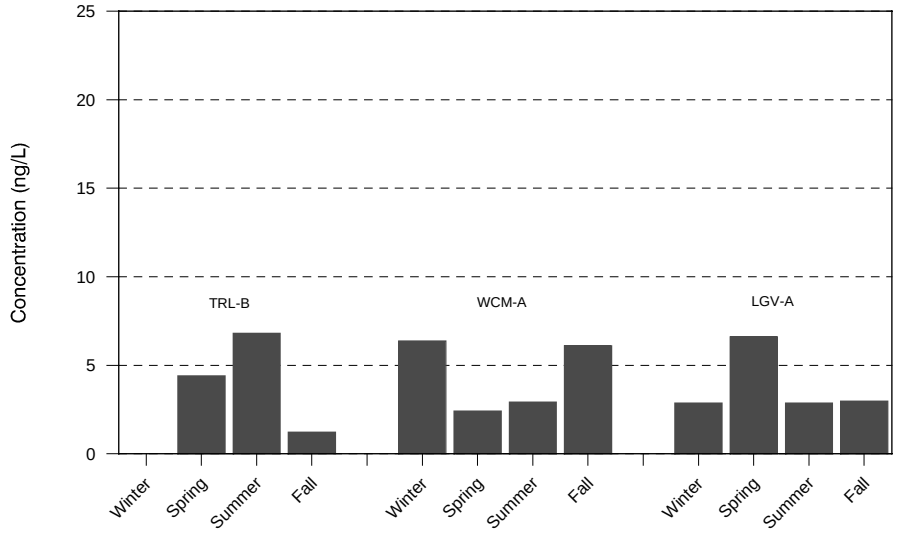


Figure 10b Seasonal precipitation weighted concentration (ng/L) for 1995. Only those sampling trains with ≥ 75% data capture (n ≥ 39) for the entire three year period are included.

Figure 10c

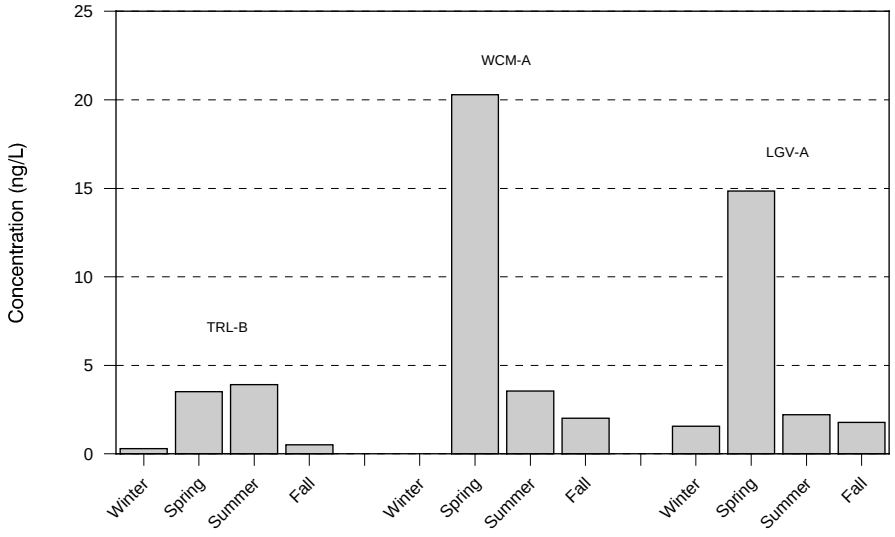


Figure 10c Seasonal precipitation weighted concentration (ng/L) for 1996. Only those sampling trains with ≥ 75% data capture (n ≥ 39) for the entire three year period are included.

Figure 10d

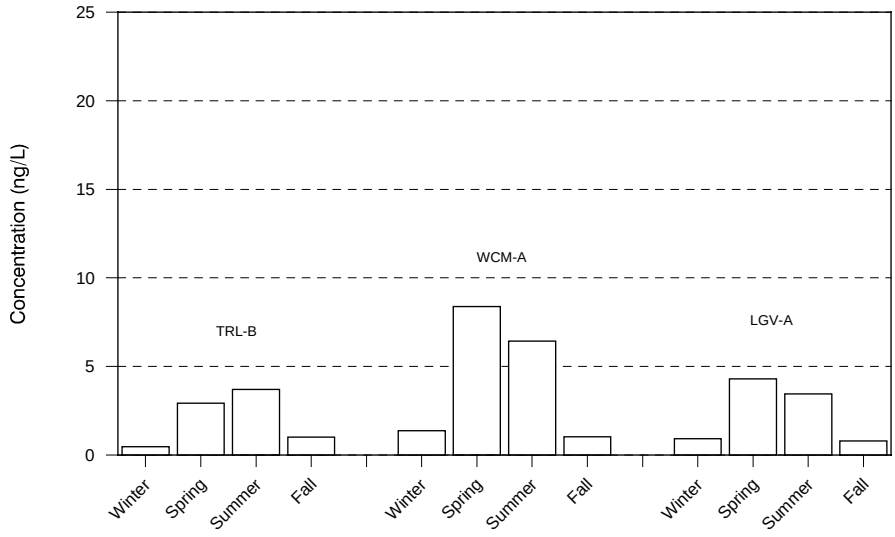


Figure 10d Seasonal precipitation weighted concentration (ng/L) for 1997. Only those sampling trains with ≥ 75% data capture (n ≥ 39) for the entire three year period are included.

Weekly Deposition

Weekly deposition was graphed for the three sites (Fig. 11a-11c). It is evident that the data demonstrate seasonal variations. There appears to be a seasonal periodicity in the data. The lowest weekly deposition values generally occur in the winter and fall, and the highest values occur in the spring and summer at all three sites. Certain years seem to have a secondary peak in the spring providing grounds for future statistical analysis.

Figure 11a

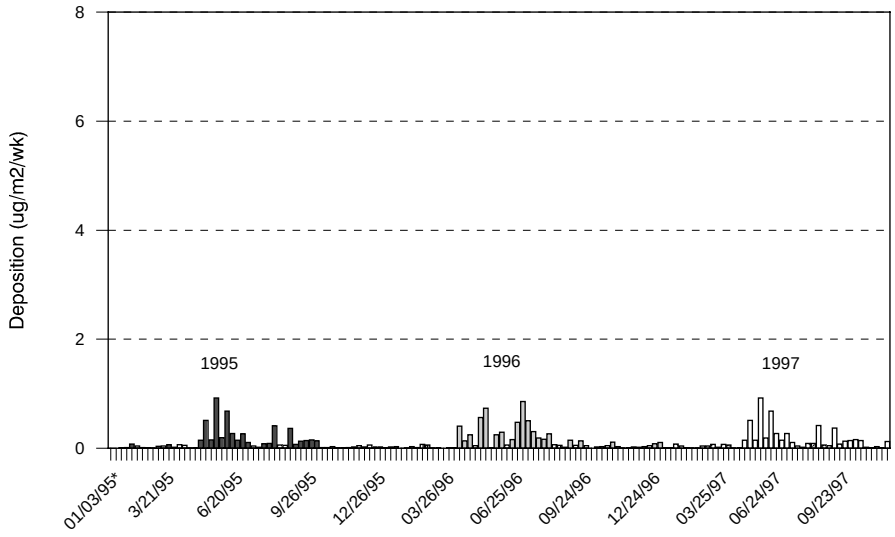


Figure 11a Trout Lake-B weekly deposition (µg/m^2/wk) values for the 1995-1997 sampling period.

Figure 11b

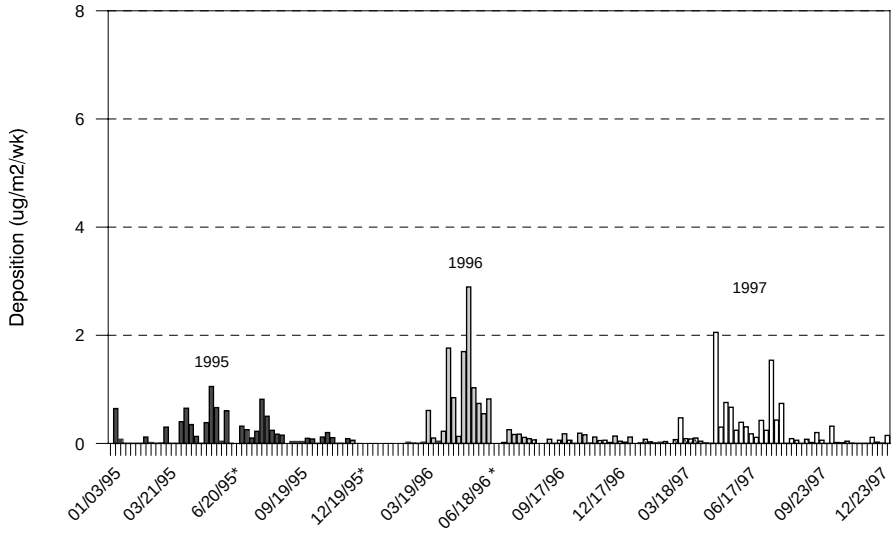


Figure 11b Wildcat Mountain-A weekly deposition (µg/m^2/wk) values for the 1995-1997 sampling period.

Figure 11c

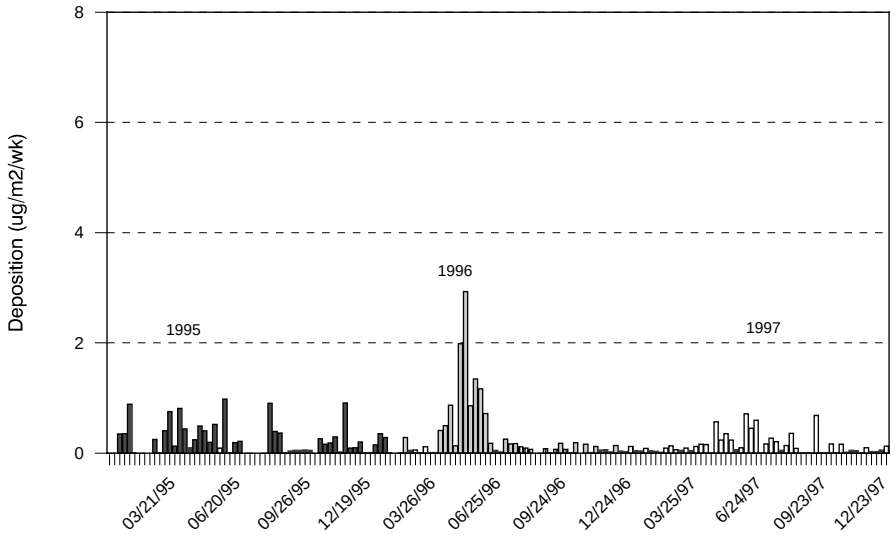


Figure 11c Lake Geneva-A weekly deposition ($\mu g/m^2/wk$) values for the 1995-1997 sampling period.

Precipitation and Concentration Comparisons

The 1997 data from the Trout Lake B-sampling train was chosen to demonstrate seasonal values of precipitation and concentration (Fig. 12a-12d). There is no steadfast statistical relationship between precipitation and concentration. There are large variations in both, and sometimes they appear to be inversely related. However, there are occasions during which both are elevated or both have low concentrations.

Figure 12a

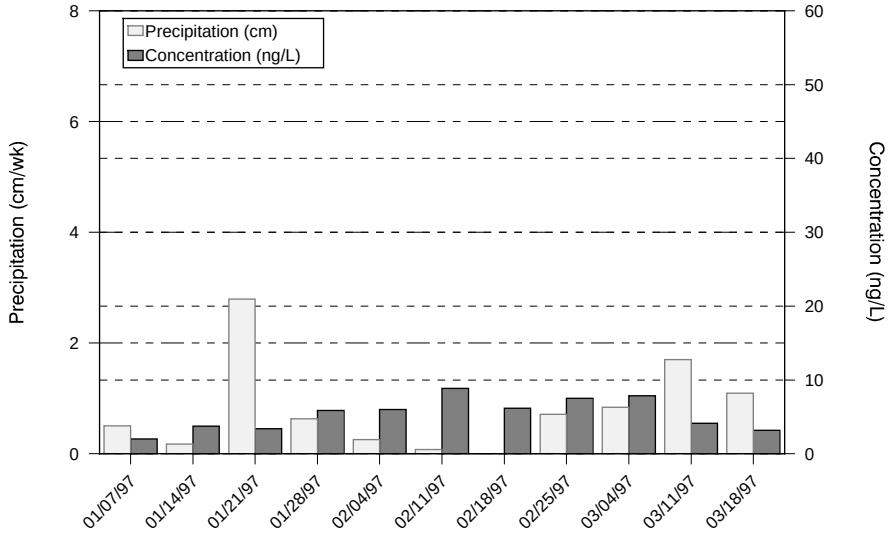


Figure 12a Trout Lake-A 1997 winter precipitation (cm/wk) and mercury sample concentration (ng/L).

Figure 12b

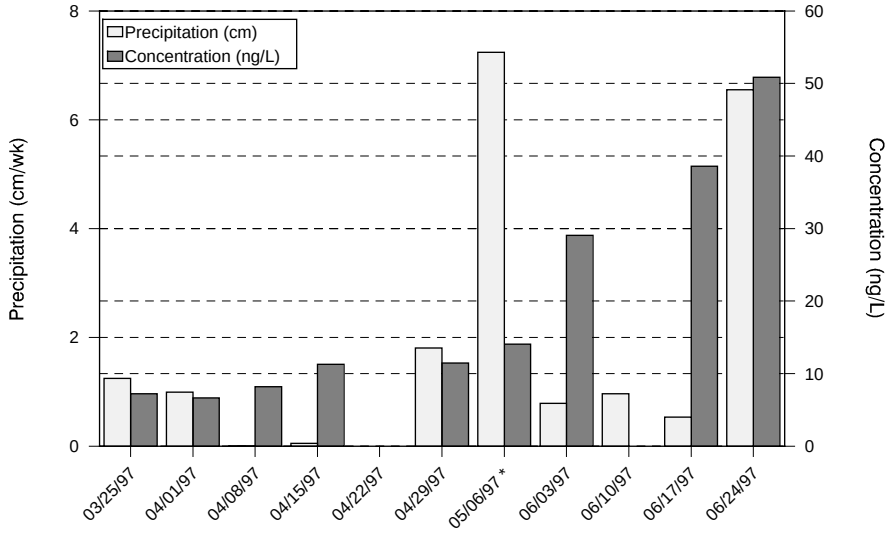


Figure 12b Trout Lake-A 1997 spring precipitation (cm/wk) and mercury sample concentration (ng/L). * 05/06/97 is a three-week sample.

Figure 12c

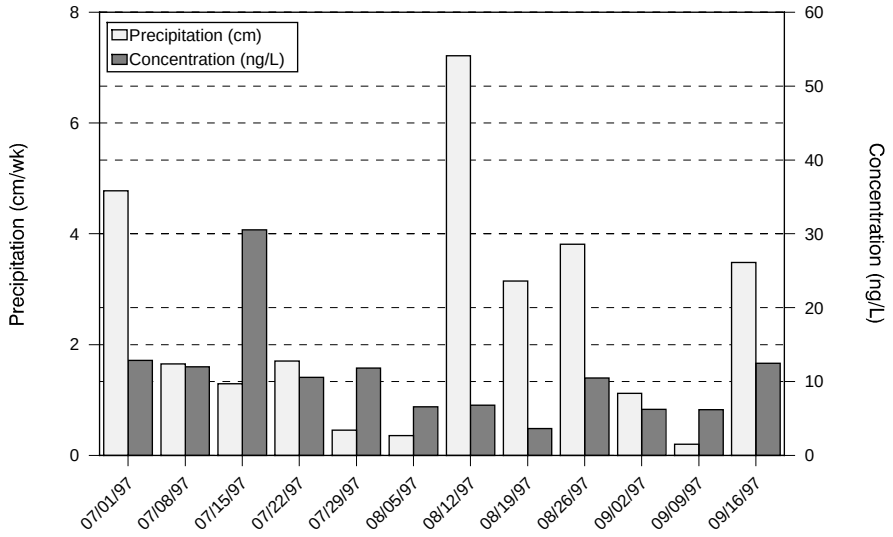


Figure 12c Trout Lake-A 1997 summer precipitation (cm/wk) and mercury sample concentration (ng/L).

Figure 12d

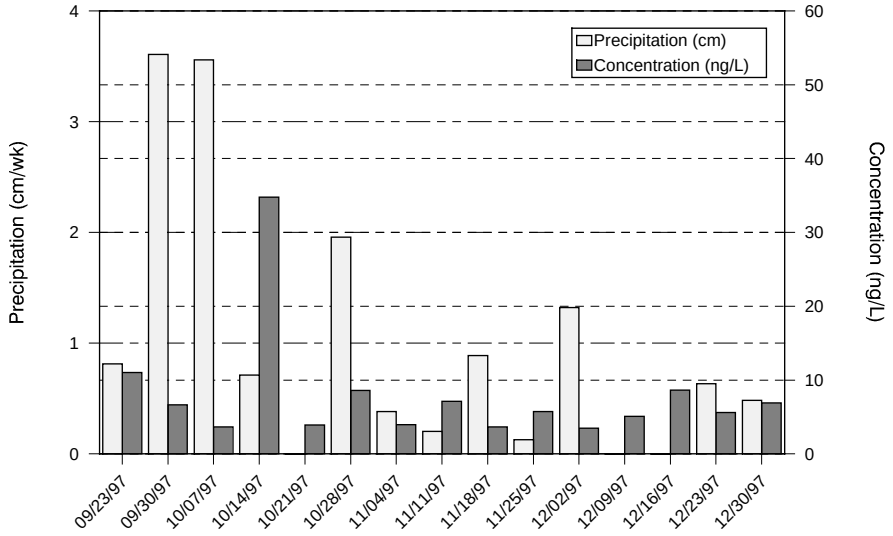


Figure 12d Trout Lake-A 1997 fall precipitation (cm/wk) and mercury sample concentration (ng/L).

WISCONSIN IVL DATA COMPARED WITH THE NATIONAL MERCURY DEPOSITION NETWORK DATA

The Wisconsin IVL mercury monitoring network and the nationwide Mercury Deposition Network (MDN) have monitors collocated at three sites in the State of Wisconsin. The sites are Brule River in Douglas County, Trout Lake in Vilas County, and Lake Geneva in Walworth County (Map).

In 1996 and 1997, less than 55% of the data is available for the WIVL network at Brule River. This is due to sample freezing in the sampling train. For this reason, only the Trout Lake and Lake Geneva sites are compared here.

There are two full years of WIVL and MDN data at the Trout Lake site and greater than 75% of the annual data is complete for both sampling trains. The following tables demonstrate that the WIVL-B sampling train and the MDN provide very similar results. There are no significant differences between mean weekly concentration or deposition values. Total deposition and precipitation vary slightly possibly due to sample size differences.

Table 6a: Trout Lake-B 1996: WIVL-B vs. MDN

Statistic	WIVL-B	MDN
Count	50	45
Mean Weekly Concentration (ng/L)	9.64±4.89	9.83±1.91
Mean Prec. Weighted Conc (ng/L)	8.48	8.73
Mean Weekly Deposition ($ug/m^2/wk$)	0.14±0.055	0.17±0.066
Total Deposition ($ug/m^2/yr$)	7.05	7.69
Total Precipitation (cm/yr)	83.11	88.7

Table 6b: Trout Lake 1997: WIVL-A vs. MDN

Statistic	WIVL	MDN
Count	47	46
Mean Weekly Concentration (ng/L)	10.32±2.94	13.02±5.72
Mean Prec. Weighted Conc (ng/L)	13.17	11.01
Mean Weekly Deposition ($ug/m^2/wk$)	0.20±0.148	0.18±0.062
Total Deposition ($ug/m^2/yr$)	9.59	8.18
Total Precipitation (cm/yr)	72.8	74.3

The MDN monitor was installed at Lake Geneva on 1/7/97 and therefore, a comparison is made only for the 1997 monitoring year. Statistically, the WIVL and MDN measurements are the same. There are minor differences in precipitation weighted concentration and total deposition values, however, they are very similar.

Table 6c: Lake Geneva 1997: WIVL-A vs. MDN

Statistic	WIVL	MDN
Count	51	43
Mean Weekly Concentration (ng/L)	10.28±1.83	13.73±3.66
Mean Prec. Weighted Conc (ng/L)	9.67	10.52
Mean Weekly Deposition ($ug/m^2/wk$)	0.14±0.05	0.17±0.06
Total Deposition ($ug/m^2/yr$)	7.19	7.48
Total Precipitation (cm/yr)	74.3	74.3

Future Sampling Plans

Due to a lack of funding, sampling with the Wisconsin IVL mercury monitor was discontinued at all sites on March 31, 1999. Currently, there is no plan to resume monitoring, and priority has been placed on the national Mercury Deposition Network consisting of four sites located at Brule River, Trout Lake, and Popple River in northern Wisconsin and Lake Geneva in southern Wisconsin.

If funding were to resume, it would be recommended that site locations be reconsidered. It is felt that a new site in northwestern Wisconsin is imperative to a better understanding of mercury deposition in the state. A WIVL site in Somerset (St. Croix County) would improve the network distribution.

Further Information:
Please contact Mr. Mark K. Allen for further information related to this report. His phone number at the WDNR is (608) 266-8049.

Additional information about the other monitoring programs of the Air Management Bureau of the WDNR is located at: http://www.dnr.state.wi.us/org/aw/air/index.htm

APPENDIX 1

Monitoring sites in the Wisconsin Mercury Deposition Monitoring Network arranged northwest to southeast	
Brule River (BRU)	The site is located on the Lake Superior shoreline near the outlet of the Brule River approximately 25 miles east of Duluth, MN. The site was established in 1994 for the collection of data on toxic deposition and was a satellite site during the Lake Michigan Mass Balance study. The site continues to be used for the collection of organic and inorganic atmospheric deposition, including mercury. In addition to the IVL type sampler, the site has wet-only sampling equipment used for the national Mercury Deposition Network (MDN). The site has also been used to study the uptake of mercury by lichens.
Trout Lake (TRL)	Trout Lake is a remote site in northern Wisconsin located near Boulder Junction and the Michigan Upper Peninsula. Located near the University of Wisconsin Limnology Center, the area has been heavily studied for the effects of mercury and acid deposition. An NADP site was established at Trout Lake in 1980 for the study of acid deposition. In addition to the IVL type sampler, the site has wet-only sampling equipment used for the national Mercury Deposition Network (MDN). The site has been used for the study of mercury uptake by lichens. Ambient ozone monitoring is also performed at this site.
Suring (SUR)	Suring is located in northeastern Wisconsin near the southern edge of the Nicolet National Forest. The site was established in 1985 as an NADP site for the study of acid deposition. The site has been used for the study of mercury uptake by lichens.
Lake DuBay (LDB)	Lake DuBay is located between the cities of Steven's Point and Wausau and is the most centrally located site in the network. The site was established as an NADP site in 1982 for the study of acid deposition. The site has been used for the study of mercury uptake by lichens. Ambient ozone and meteorology measurements are also performed at this site.
Wildcat Mountain (WCM)	A remote site located in west central Wisconsin. Established as an NADP site in 1989 for the study of acid deposition. Other studies at the site include the uptake of mercury by lichens and aspen clones. The site also serves as a background for tropospheric ozone. Ambient ozone and meteorology measurements are also performed at this site.
Devils Lake (DVL)	The Devils Lake site is located in the south central region of Wisconsin. The site is within a state park and was established to locate possible mercury inputs to Devils Lake, a popular recreation lake. Located in the unique geological features of the Baraboo Range, this site is also used as a background for ozone and oxides of nitrogen studies. Meteorology measurements are also performed at this site.
Lake Geneva (LGV)	Lake Geneva is the located in southern Wisconsin. The site is the closest to heavily developed areas in northern Illinois and southeastern Wisconsin. The site was established as an NADP site in 1984 for the study of acid deposition. Other studies conducted at the site include the uptake of mercury by lichens and aspen clones. The site is also part of Wisconsin and meteorology ozone monitoring network. In addition to the WIVL sampler, this site has wet-only mercury sampling equipment used for the national Mercury Deposition Network (MDN).

APPENDIX 2A

Measured mercury concentrations [Hg] in samples with <0.127 cm (< 0.05 in.) precipitation

Network	Sampler	n =	Mean [Hg] (ng/L)	95% Conf. Interval
1996 WMDN	A	24	21.17	13.7-28.7
1996 WMDN	B	25	6.22	4.5-7.9
1996 Trout Lake	A	2	16.16	-3.4-35.7
1996 Trout Lake	B	4	6.45	3.4-9.5
1997 Trout Lake	A	7	8.60	5.39-11.81
1997 Trout Lake	B	5	76.92	-57.6-211.44
1997 Trout Lake*	B	4	8.30	4.59-12.01

* - This excludes an anomalous B-sample at Trout Lake from 04/22/97 with a Hg concentration of 351.4 (ng/L) and a 0.04 (in) of precipitation.

APPENDIX 2B

Sample collection precision data as Relative Percent Difference (RPD) for precipitation samples >0.127 cm (> 0.05 in.)

	1996 All Sites	1997 Trout Lake
n	202	38
Mean RPD	17.4%	10.2%
Median PRD	4.2%	2.7%
Maximum RPD	377.8%	164.3%
Minimum RPD	0.0%	0.1%

Duplicate samples were collected at all sites in 1996, but only at Trout Lake in 1997.

APPENDIX 3A

Sample collection completion expressed as a percentage of expected samples. Completion data is reported for the year and each quarter of the year.

Sites	BRULE	DUBAY	DEVILS	GENEVA	SURING	WILDCAT	TROUT
1995	53.8	92.3	71.2	100.0	98.1	94.2	100.0
1	23.1	84.6	23.1	100.0	100.0	100.0	100.0
2	69.2	92.3	92.3	100.0	100.0	100.0	100.0
3	76.9	92.3	100.0	100.0	92.3	100.0	100.0
4	46.2	100.0	69.2	100.0	100.0	76.9	100.0
1996	26.9	69.2	11.5	98.1	100.0	86.5	100.0
1	0.0	46.2	7.7	1.0	100.0	46.2	100.0
2	0.0	92.3	0.0	100.0	100.0	100.0	100.0
3	91.7	100.0	0.0	91.7	100.0	100.0	100.0
4	21.4	42.9	35.7	100.0	100.0	100.0	100.0
1997	51.9	59.6	96.2	96.2	98.1	96.2	94.2
1	0.0	8.3	91.7	100.0	100.0	83.3	100.0
2	7.7	76.9	100.0	92.3	92.3	100.0	76.9
3	92.9	78.6	92.9	100.0	100.0	100.0	100.0
4	100.0	69.2	100.0	92.3	100.0	100.0	100.0

Cases where the sampling period was extended to two weeks do to a lack or shortage of glassware do not appear above. These samples were sometimes retained for purposes of annual averages.

APPENDIX 3B

Summarized inter-laboratory results				
	N	Mean	Median	95% Conf. Interval
1996 Network				
SLOH Hg (ng/L)	209	16.83	11.4	13.73-19.92
Limnology Hg (ng/L)	209	11.06	6.6	8.75-13.27
Lab RPD	209	49.4%	57.7%	------
1996 Trout Lake				
SLOH Hg (ng/L)	29	7.13	6.88	5.75-8.52
Limnology Hg (ng/L)	29	4.87	4.5	3.76-5.98
Lab RPD		37.2%	33.4%	--------
1997 Trout Lake				
SLOH Hg (ng/L)	40	11.0	7.2	7.68-14.30
Limnology Hg (ng/L)	40	8.35	5.72	6.14-10.56
Lab RPD	40	22.5%	20.2%	

APPENDIX 3C

Summarized inter-network comparisons results - 1996 Trout Lake				
	N	Mean	Median	95% Confidence
WIVL Hg (ng/L)	85	8.7	6.3	5.9-11.6
MDN Hg (ng/L)	44	10.0	9.00	8.2-11.9
WIVL Deposition (ng/M2/yr)	85	134.84	59.1	98.6-171.1
MDN Hg (ng/M2/yr)	44	173.7	89.6	108.0-239.4

APPENDIX 4A

Wisconsin mercury summary statistics for 1995								
Site	*n*[a]	% of 52 samples collected	Precip. Amt (cm/yr)	Mean Weekly Precip (cm/wk)	Total Hg Deposition ($\mu g/m^2/yr$)	Mean Weekly Hg Deposition ($\mu g/m^2/wk$)	Mean Weekly Hg Conc. (ng/L)	Mean PWC [b] (ng/L)
*BRU-A	22	42	56.26	2.16	5.39	0.21	15.51	9.58
*BRU-B	24	46	56.39	2.09	5.37	0.20	14.72	9.52
*TRL-A	23	44	41.61	1.81	3.65	0.16	19.82	8.77
TRL-B	43	83	78.18	1.82	10.01	0.23	19.42	12.8
*SUR-A	36	69	50.22	1.17	10.58	0.25	98.66	21.06
SUR-B	45	87	72.49	1.39	10.53	0.20	58.34	14.53
LDB-A	40	77	73.86	1.64	9.98	0.22	41.52	13.51
*LDB-B	38	73	66.70	1.48	8.19	0.18	31.71	12.23
WCM-A	40	77	69.82	1.52	9.20	0.20	25.08	21.20
WCM-B	42	81	71.91	1.50	13.10	0.27	42.88	18.22
*DVL-A	38	73	82.50	2.17	13.91	0.37	19.24	16.86
*DVL-B	37	71	79.65	2.10	10.22	0.27	17.90	12.83
LGV-A	42	81	78.11	1.86	11.96	0.28	28.52	15.31
LGV-B	48	92	84.51	1.76	12.42	0.26	31.63	14.69
Mean	37	71	68.73	1.75	9.61	0.24	33.21	14.37
Range	22-48	42-92	56.26-84.51	1.17-2.17	3.65-13.91	0.16-0.37	15.51-98.66	8.77-21.2

Table of summary statistics includes suspect data points and excludes C sampling train data

* - indicates sites with less than 75% of total possible samples collected

a – indicates lesser of concentration or precipitation sample size

b – (PWC) is precipitation weighted concentration (ng/L)

APPENDIX 4B

Wisconsin mercury summary statistics for 1996

Site	n	% of 52 samples collected	Precip. Amt (cm/yr)	Mean Weekly Precip. (cm/wk)	Total Hg Deposition (ug/m2/yr)	Mean Weekly Hg Deposition (ug/m2/wk)	Mean Weekly Hg Conc (ng/L)	Precip. weighted mean [Hg] (ng/L)
*BRU-A	12	23	27.56	2.30	2.75	0.230	11.31	10.00
*BRU-B	16	31	30.10	1.88	1.78	0.111	6.66	5.91
TRL-A	33	63	57.20	1.73	4.30	0.130	7.74	7.52
TRL-B	51	98	83.93	1.72	7.16	0.138	9.37	8.01
SUR-A	43	83	82.63	1.88	13.05	0.297	16.97	15.79
SUR-B	46	88	83.39	1.77	8.93	0.190	11.76	10.39
*LDB-A	8	15	7.24	0.90	0.55	0.068	8.64	7.55
*LDB-B	9	17	10.46	1.16	0.66	0.073	5.98	6.28
WCM-A	42	81	54.23	1.23	13.88	0.330	26.65	25.60
WCM-B	44	85	62.61	1.39	8.65	0.192	16.24	13.81
DVL-A	37	71	66.95	1.81	7.71	0.208	11.86	11.52
DVL-B	38	73	67.16	1.72	5.68	0.146	14.60	8.46
LGV-A	51	98	75.64	1.48	15.55	0.305	18.16	20.56
LGV-B	49	94	75.08	1.50	7.80	0.156	10.98	10.39
Mean	34	65	56.01	1.61	7.03	0.184	12.66	11.56
Range	8-51	15-98	7.24-83.93	1.05-1.76	0.546-15.55	0.068-0.330	5.98-26.65	6.28-25.60

Table of summary statistics includes suspect data points
* - indicates sites with less than 75% of total possible samples collected
a – indicates lesser of concentration or precipitation sample size
b – (PWC) is precipitation weighted concentration (ng/L)

APPENDIX 4C

Wisconsin mercury summary statistics for 1997

Site	n	% of 52 samples collected	Precip. Amt (cm/yr)	Mean Weekly Precip. (cm/wk)	Total Hg Deposition (ug/m2/yr)	Mean Weekly Hg Deposition (ug/m2/wk)	Mean Weekly Hg Conc (ng/L)	Precip. weighted mean [Hg] (ng/L)
BRU	29	56	30.48	1.05	3.22	.111	10.71	10.57
TRL-A	47	90	71.88	1.52	6.26	.136	10.32	13.35
TRL-B	43	83	70.59	1.64	5.71	.136	10.45	8.09
SUR	51	98	62.18	1.22	6.59	.128	11.15	10.59
LDB	51	98	57.18	1.12	7.05	.138	14.06	12.33
WCM	49	94	61.65	1.26	10.75	.220	14.08	17.45
DVL	45	87	79.27	1.76	8.98	.199	10.41	11.33
LGV	51	98	74.30	1.46	7.19	.141	10.28	9.67
Mean	45.75	88	63.44	1.38	6.99	.151	11.43	11.67
Range	29-51	56-98	30.48-79.27	1.05-1.76	3.22-10.75	.111-.220	10.28-14.08	8.09-17.45

Table of summary statistics includes suspect data points
* - indicates sites with less than 75% of total possible samples collected
a – indicates lesser of concentration or precipitation sample size
b – (PWC) is precipitation weighted concentration (ng/L)

APPENDIX 5

DEFINITIONS

Concentration

Precipitation Weighted Concentration:
The precipitation-weighted concentration, also known as the volume weighted concentration, is a process, which normalizes the weekly concentration values for the amount of precipitation. The formula for calculating precipitation weighted concentration is:

$$\sum \{(X*Y)/Z\}$$

where: X = weekly concentration value (ng/L)
Y = weekly precipitation value (cm)
Z = annual total precipitation (cm)

Confidence Intervals (95% CI):
The confidence interval allows one to estimate, with a 95% degree of confidence, the range within which the mean may lie. The formula used for the confidence interval is:

$$\bar{x} - T_{n-1,\alpha/2}(s/n^{1/2}) \leq \mu \geq \bar{x} + T_{n-1,\alpha/2}(s/n^{1/2})$$

where: $\bar{x}$ = the sample mean
T = the T distribution
α = the tail value; here it is 0.5
s = the sample variance
n = the sample size
μ = the population mean
The confidence interval is useful because it gives information on the precision of the estimate of the mean.

Deposition

Annual Statewide Mean Deposition:
The statewide mean deposition is the average of all valid weekly deposition values from all samplers for a given year. It gives us an estimate of the average amount of mercury deposited across the state in a given year. This is calculated by summing the weekly deposition values from all sampling trains meeting the data completeness criterion and dividing this sum by the total number of samples collected.

Deposition

The deposition of mercury is calculated from the weekly concentration and precipitation values monitored at each site. A weekly concentration in ng/cm^3 is multiplied by the weekly precipitation (cm) value. Next, unit analysis is used to get the final units into ug/m^2. The process is as follows:

[weekly Hg concentration (ng/cm^3)] * [(cm) of weekly precipitation] * [ug/1000 ng] * [10^4 (cm^2/m^2)] = ug/m^2

Deposition is given in units of mass per unit area.

Mean Weekly Deposition
The mean weekly deposition is the average amount of atmospheric mercury deposited to the earth on a weekly basis. The mean weekly deposition is calculated by averaging the deposition values for an entire year based on the number of valid samples. For example, if 45 samples were collected for the 1997 monitoring year with the Lake Geneva A-sampling train, the weekly deposition values would be summed and then divided by 45 to obtain the *mean weekly deposition*.

Total Deposition
Total deposition is the sum of all available weekly deposition values over a year's time, and it is measured in $\mu g/m^2$. The total deposition value gives the amount of atmospheric mercury that is deposited to the earth at an individual site over the course of an entire year.

Intra-site variability The variation during a period within an individual site.

Inter-site variability The variation that exists among sites.

On-line Date The date on which a new, clean sample bottles is placed in the WIVL sampler for sample collection.

Reactive Gaseous Mercury (RGM) the water-soluble compounds of Hg that exist in flue gases from combustion processes. RGM compounds may be associated with particles or occur as gases. Some of the gases are a) HgCl2 b) HgBr2 c) Hg (OH) 2 or compounds of other halides (Group VIIA periodic chart). RGM species are highly water-soluble (10^5 times more soluble than Hg^0). Solubility strongly influences RGM removal processes and deposition rates from the atmosphere.

The following is a list of pertinent atmospheric transformations of mercury.
1) Oxidation of Hg^0 to Hg^{2+} by reaction with ozone, OH^{-1} (hydroxyl radical) or H_2O_2 (hydrogen peroxide) in cloudwater
2) Reduction of Hg^{2+} to Hg^0 by reaction with $SO_{2\,(g)}$ or $SO_3^{2-}{}_{(aq)}$
3) Direct oxidation of Hg^0 to Hg^{2+} by reaction with O_3 in the gas phase

Understanding of these reactions is crucial to modeling RGM. Although Hg^0 is the dominant form of atmospheric Hg, even trace amounts of RGM species may control the overall deposition of Hg (3).

Season
Each WIVL season:

1) begins within a week after the calendar date of the true season's beginning. The true season begins on either an equinox or solstice as follows; (beginnings of season vary):
   a) spring equinox (March 20-23)
   b) summer solstice (June 20-23)
   c) autumnal equinox (September 20-23)
   d) winter solstice (December 20-23)
2) contains 13 weeks
3) Example: a WIVL season begins within a week after the calendar date of the season's beginning. That is, if a season begins on 06/21/99, the WIVL season begins within a week after 06/21/99.

Total Gaseous Mercury (TGM) Sum of all mercury in the gaseous phase. This includes both the ionic form (Hg^{2+}) and the elemental vapor form of Hg. While all gaseous forms of mercury are included, the TGM is dominated by the elemental vapor form in the atmosphere due to its lack of reactivity.

Year
Calendar year over which data is average or summed. For this report a year would include for samples beginning with first on-line date and ending with the last on-line date of the year.

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